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Sir C. V. RAMAN, Kt., M.A., Ph.D., D.Sc., LL.D., F.R.S., N.L.

(With Thirtysix Plates)

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Contents of Vol. VII

PART I.

PAGE.

1. Surface Convection and Variation of Temperature near a Hot Surface—By L. A. Ramdas and S. L. Malurkar .. 1
2 Magnetic Rotations of Liquid Mixtures—By Ram Narain Mathur and Amar Nath Kapur 15
3. The Diamagnetism and Structure of some Compounds of Ethylene, Carbon Tetrachloride and Titanium Tetrachloride—By V. I. Vaidhianathan and Balwant Singh ... 19
4. On the 'Performance Test' in Statistics—By S. R. Savur ... 27
5. The Diamagnetism of Bismuth—By S. Ramchandra Rao ... 35
6. X-ray Analysis of the Structure of Diphenyl—By Jagattaran Dhar 43
7. On the Raman Spectra of Piperidine, Ethyl Alcohol and Acetone—By S. C. Sirkar 61
8. Ploarisation of Raman Lines in Liquids—By S. Bhagavantam 79
9. A Note on the Variation of Faraday Effect with Concentration —By P. K. Pillai 87
10. Note on a New Rotating Commutator—By Prof. A. Venkat Rao Telang 91
11 A Note on the Coefficient of Viscosity of Liquid Sodium Amalgams—By G. R. Paranjpe 95

Review—The Physical Properties of the Soil—By Dr. Bernard A. Keen 99

The Institute of Physics 103

PART II.

12. Evidence for a Spinning Photon: I. Intensity Relations in the Raman Spectrum of Hydrogen—By S. Bhagavantam ... 107
13. Light-scattering in relation to Molecular Structure: New Data for Depolarisation in 39 Gases—By S. Parthasarathy 13
14. Modern Differential Geometries—By D. D. Kosambi ...

PART III.

PAGE.

15. On Discontinuous Fluid Motion under Different Thermal Conditions—By Sudhansu Kumar Banerji and Vishnu Madhab Ghatage 165
16. On the Measurement of the Absorption Coefficient of Some Indian Materials—By S. Kalyanraman 229
17. Are Argon and Methane Molecules Optically Anisotropic?—By S. Parthasarathy 243
18. A Generalised Formula in the New Statistics—By M. K. Gopalaiengar 251
19. On the Raman Spectra of Di-methyl Ether, Di-ethyl Ether and Heptane—By S. C. Sirkar 257
2 New Lines in the Absorption Spectra of the Alkalies—By Snehamoy Datta and Birendra Kumar Chakravarty ... 273
A New Steel Flooring 283

PART IV.

21. The Raman Spectra of Iodides, Part I, Phosphonium Iodide and Methyl Iodide—By N. Gopal Pai 285
22. The Spark Spectrum of Arsenic—By Mela Ram 299
23. Transmission of Light through Suspensions of Powdered Crystals—By Baidyanath Mukhopadhyay 307
24. Magnetic Birefringence in Solutions of Sodium Chlorate and Sodium Bromate—By S. W. Chinchalkar 317
25. Electronic Constitution of Some Simple and Complex Derivatives of Copper in Relation to their Magnetic Properties —By S. S. Bhatnagar, Balwant Singh and Abdul Ghani 323
26. Annual Report for 1931 331

PART V.

27. Molecular Rotation in Liquids as revealed by the Raman Effect—By S. P. Ranganadham 353
28. Experimental Study of the Duration of Contact of an Elastic Hammer striking a Damped Pianoforte String—By Mohinimohan Ghosh 365
29. Note on an Improved Form of an Induction Coil Buzzer—By H. Mukherjee 383

PAGE.

30. The Effect of the Indian Mountain Ranges on Air Motion—By S. R. Savur 389
31. Susceptibility of liquid Mixtures with a New Apparatus—By L. Sibaiya and H. S. Venkataramiah 393
32. A Note on the General Spectrum of the Night Sky as observed in India—By K. R. Ramanathan 405
33. The Effect of the Indian Mountain Ranges on Air Motion—By S. K. Banerji 411
34. A Note on the Shape of the Electro-capillary Curve of Mercury in Capillary Inactive Electrolytes—By R. M. Joshi 427
35. A Bibliography of the Raman Effect, 1930-32—By S. C. Sirkar 431

PART VI.

36. Magnetic Birefringence in Liquid Mixtures—By S. W. Chinchalkar 491
37. Raman Spectra of Iodides: Part II. Ethyl, Propyl and Isobutyl Iodides—By N. Gopal Pai 519
38. The New Statistics and Electrostatics—By M. K. Gopalaiengar 531
39. The Vibrations of the Different Parts of the Pianoforte Soundboard—By L. D. Mahajan 539
40. Intensity Relations in the Raman Spectrum of Hydrogen: II —By S. Bhagavantam 549
41. Further Investigations of the First Spark Spectrum of Arsenic —By A. S. Rao 561
42. The Raman Spectra of Pinene, Thiophene, Salol and Thymol —By S. Venkataswaran and S. Bhagavantam ... 585
43. Calculation of the Second Virial Coefficient of Gases—By T. S. Wheeler 595
44. Evidence for the Cybotactic Group View of the Interior of a Liquid—By G. W. Stewart 603
45. Electric Polarisability and Diamagnetic Susceptibility of Molecules—By S. Bhagavantam 617

Title-page, Contents and Index.

AUTHOR INDEX

		PAGE.
Abdul Ghani ...	(See Bhatnagar, S. S.)	
Banerji, S. K. ...	The Effect of the Indian Mountain Ranges on Air Motion	411
Banerji, S. K. and Ghatage, V. M.	On Discontinuous Fluid Motion under Different Thermal Conditions ...	165
Bhagavantam, S. ...	Polarisation of Raman Lines in Liquids...	79
	Evidence for a Spinning Photon: I. Intensity Relations in the Raman Spectrum of Hydrogen	107
	Intensity Relations in the Raman Spectrum of Hydrogen: II	549
	Electric Polarisability and Diamagnetic Susceptibility of Molecules	617
	(See Venkateswaran, S.)	
Bhatnagar, S. S., Singh, Balwant and Abdul Ghani.	Electronic Constitution of Some Simple and Complex Derivatives of Copper in relation to their Magnetic Properties...	323
Chakravarty, Birendrakumar.	(See Datta, Snehamoy).	
Chinchalkar, S. W. ...	Magnetic Birefringence in Solutions of Sodium Chlorate and Sodium Bromate	317
	Magnetic Birefringence in Liquid Mixtures...	491
Datta, Snehamoy and Chakravarty, Birendrakumar.	New Lines in the Absorption Spectra of the Alkalies	273
Dhar, Jagattaran ...	X-ray Analysis of the Structure of Diphenyl	43
Ghatage, V. M. ...	(See Banerji, S. K.)	
Ghosh, Mohinimohan...	Experimental Study of the Duration of Contact of an Elastic Hammer striking a Damped Pianoforte String ...	365

		PAGE.
Gopalaiengar, M. K.	A Generalised Formula in the New Statistics	251
	The New Statistics and Electrostatics ...	531
Joshi, R. M.	A Note on the Shape of the Electro-capillary Curve of Mercury in Capillary Inactive Electrolytes	427
Kalyanaraman, S. ...	On the Measurement of the Absorption Co-efficient of Some Indian Materials ...	229
Kapur, Amarnath ...	(See Mathur, R. N.)	
Kosambi, D. D. ...	Modern Differential Geometrics ...	159
Mahajan, L. D. ...	The Vibrations of the Different Parts of the Pianoforte Sound-board	539
Malurkar, S. L. ...	(See Ramdas, L. A.)	
Mathur, R. N. and Kapur, Amar Nath.	Magnetic Rotations of Liquid Mixtures	15
Mela Ram ...	The Spark Spectrum of Arsenic ...	299
Mukherjee, H. ...	Note on an Improved Form of an Induction Coil Buzzer	383
Mukhopadhyay, Baidyanath.	Transmission of Light through Suspensions of Powdered Crystals ...	307
Pai, N. Gopal ...	The Raman Spectra of Iodides, Part I, Phosphonium Iodide and Methyl Iodide	285
	Raman Spectra of Iodides, Part II, Ethyl Propyl and Isobutyl Iodides ...	519
Paranjpe, G. R. ...	A Note on the Coefficient of Viscosity of Liquid Sodium Amalgams ...	95
Parthasarathy, S. ...	Light-scattering in relation to Molecular Structure: New data for Depolarisation in 39 Gases	139
	Are Argon and Methane Molecules Optically Anisotropic ?	243
Pillai, P. K. .	A Note on the Variation of Faraday Effect with Concentration	87
Ramanathan, K. R. .	A Note on the General Spectrum of the Night Sky as observed in India ...	405
Ramdas, L. A.	Surface Convection and Variation of Temperature near a Hot Surface ...	1
Ranganadham, S. P.	Molecular Rotation in Liquids as revealed by the Raman Effect	353

		PAGE.
Rao, A. S. ..	Further Investigations of the First Spark Spectrum of Arsenic	561
Rao, S. ...	The diamagnetism of Bismuth ...	35
Ramachandra Savur, S. R.	On the "Performance Test" in Statistics	27
	The Effect of the Indian Mountain Ranges on Air Motion	389
Sibaiya, L. and Venkataramiah, H. S.	Susceptibility of Liquid Mixtures with a New Apparatus	393
Singh, Balwant ...	(See Vaidhianathan, V. I.) (See Bhatnagar, S. S.)	
Sirkar, S. C. ...	On the Raman Spectra of Piperidine, Ethyl Alcohol and Acetone	61
	On the Raman Spectra of Dimethyl Ether, Diethyl Ether and Heptane ...	257
	A Bibliography of the Raman Effect 1930-32	431
Stewart, G. W. ...	Evidence for the Cybotactic Group View of the Interior of a Liquid	603
Telang, Prof. A. Venkata Rao.	Note on a Rotating Commutator ...	91
Vaidhianathan, V. I. and Singh, Balwant.	The Diamagnetism and Structure of Some Compounds of Ethylene, Carbon Tetrachloride and Titanium Tetrachloride	19
Venkataramiah, H. S.	(See Sibaiya, L.)	
Venkateswaran, S. and Bhagawantam, S.	The Raman Spectra of Pinene, Thiophene, Salol and Thymol	585
Wheeler, T. S. ...	Calculation of the Second Virial Coefficient of Gases	595

SUBJECT INDEX

PAGE.

Absorption Coefficient:- On the Measurement of, of Some Indian Materials—S. Kalyanaraman ... 229
Absorption Spectra:— New Lines in the, of the Alkalies—Snehamoy Datta and Birendrakumar Chakravarty 273
Acetone:— (See Raman Effect)
Air Motion:- The Effect of the Indian Mountain Ranges on—S. R. Savur ... 389
The Effect of Indian Mountain Ranges on—S. K. Banerji 411
Alkalies:— (See Absorption Spectra)
Announcements:— The Institute of Physics 103
A New Steel Flooring 283
Annual Report for 1931 331
Argon:— ... (See Light-scattering)
Arsenic:— ... (See Spectra)
Bibliography of the Raman Effect, 1930-32:— ... ... S. C. Sirkar 431
Birefringence:— ... (See Magnetism)
Bismuth:— ... (See Magnetism)
Buzzer:— ... (See Induction Coil)
Carbon Tetrachloride:— (See Magnetism)
Commutator:— ... Note on a New Rotating—Prof. A. Venkata Rao Telang 91
Copper Derivatives:— ... (See Magnetism)
Crystals:— ... (See Suspensions)
Cybotactic Group View:— ... Evidence for the, of the Interior of a liquid—G. W. Stewart 603
Depolarisation in Gases:— ... (See Light-scattering)
Diamagnetic Susceptibility:— ... (See Electric Polarisability)
Diethyl Ether:— ... (See Raman Effect)
Differential Geometry:— Modern—D. D. Kosambi 159
Dimethyl Ether:— ... (See Raman Effect)

PAGE.

Diphenyl:— ... (See X-rays)

Discontinuous Fluid Motion:— ... (See Fluid Motion)

Elastic Hammer:— ... (See Pianoforte String)

Electric Polarisability:— and Diamagnetic Susceptibility of Molecules—S. Bhagavantam 617

Electro-capillary Curve:— A Note on the Shape of the, of Mercury in Capillary Inactive Electrolytes—R. M. Joshi 427

Electrostatics:— (See Statistics)

Ethyl Alcohol:— (See Raman Effect)

Ethylene:— Compounds of (See Magnetism)

Ethyl Iodide:— (See Raman Effect)

Faraday Effect:— (See Magnetism)

Fluid Motion:— On Discontinuous, under Different Thermal Conditions—S. K. Banerji and V. M. Ghatage 165

Gases:— ... (See Light-scattering)
(See Virial Coefficient)

Generalised Formula:— (See Statistics)

Hot Surface— ... (See Surface Convection)

Hydrogen:— ... (See Raman Effect)

Indian Mountain Ranges:— ... (See Air Motion)

Induction Coil Buzzer:— Note on the Improved Form of an—H. Mukherjee 383

Intensity Relations:— ... (See Raman Effect)

Isobutyl Iodide:— ... (See Raman Effect)

Light-scattering:— ... Light-scattering in relation to Molecular Structure: New Data for Depolarisation in 39 Gases—S. Parthasarathy 139
Are Argon and Methane Molecules Optically Anisotropic?—S. Parthasarathy 243

Liquid Mixtures: (See Magnetism)

Magnetism:— Magnetic Rotations of Liquid Mixtures—Ram Narain Mathur and Amarnath Kapur 15

PAGE.

The Diamagnetism and Structure of Some Compounds of Ethylene, Carbon Tetrachloride and Titanium Tetrachloride—V. I. Vaidhianathan and Balwant Singh 19
The Diamagnetism of Bismuth—S. Ramachandra Rao 35
A Note on the Variation of Faraday Effectwith Concentration—P. K. Pillai 87
Magnetic Birefringence in Solutions of Sodium Chlorate and Sodium Bromate—S. W. Chinchalkar ... 317
Electronic Constitution of Some Simple and Complex Derivatives of Copper in relation to their Magnetic Properties —S. S. Bhatnagar, Balwant Singh and Abdul Ghani 323
Susceptibility of Liquid Mixtures with a New Apparatus—L. Sibaiya and H. S. Venkataramiah 393
Magnetic Birefringence in Liquid Mixtures—S. W. Chinchalkar ... 491

Mercury :— (See Electro-capillary Curve)
Methane :— (See Raman Effect)
Molecular Rotation :— (See Raman Effect)
Mountain Ranges :— (See Air Motion)
Night Sky :— A Note on the General Spectrum of the, as observed in India—K. R. Ramanathan 405
Performance Test :— ... (See Statistics)
Phosphonium Iodide :— (See Raman Effect)
Pianoforte Sound-board :— The Vibrations of the Different Parts of the—L. D. Mahajan 539
Pianoforte String :— ... Experimental Study of the Duration of Contact of an Elastic Hammer Striking a Damped—Mohinimohan Ghosh 365
Pinene :— ... (See Raman Effect)
Piperidine :— ... (See Raman Effect)

PAGE.

Polarisation :— ... (See Raman Effect)
Powdered Crystals :— ... (See Suspensions)
Propyl Iodide :— ... (See Raman Effect)
Raman Effect :— .. On the Raman Spectra of Piperidine, Ethyl Alcohol and Acetone—S. C. Sirkar 61
  Polarisation of Raman Lines in Liquids—S. Bhagavantam ... 79
  Evidence for the Spinning Photon. I. Intensity Relations in the Raman Spectrum of Hydrogen—S. Bhagavantam 107
  On the Raman Spectra of Di-methyl Ether, Diethyl Ether and Heptane—S. C. Sirkar 257
  The Raman Spectra of Iodides, Part I. Phosphonium Iodide and Methyl Iodide—N. Gopal Pai 285
  Molecular Rotation in Liquids as revealed by the Raman Effect—S. P. Ranganadham 353
  Raman Spectra of Iodides, Part II. Ethyl, Propyl and Isobutyl Iodides—N. Gopal Pai 519
  Intensity Relations in the Raman Spectrum of Hydrogen: II—S. Bhagavantam 549
  The Raman Spectra of Pinene, Thiophene, Salol and Thymol—S. Venkateswaran and S. Bhagavantam ... 585
Review:- The Physical Properties of the Soil—By Dr. Bernard A. Keen ... 99
Salol :— ... (See Raman Effect)
Sodium Amalgam: (See Viscosity)
Sodium Bromate :- (See Magnetism)
Sodium Chlorate :- (See Magnetism)
Spectra :— (See Raman Effect; Night Sky).
  The Spark Spectrum of Arsenic—Mela Ram 299

PAGE.

Further Investigations of the First Spark Spectrumof Arsenic—A. S. Rao 561

Spinning Photon :— (See Raman Effect)

Statistics :— On the Performance Test in Statistics—S. R. Savur 27
A Generalised Formula in the New Statistics—M. K. Gopalaiengar ... 251
The New Statistics and Electrostatics—M. K. Gopalaiengar 531

Surface Convection: and Variation of Temperature near a Hot Surface—L. A. Ramdas and S. L. Malurkar 1

Susceptibility :— (See Magnetism)

Suspensions :— Transmission of Light through, of Powdered Crystals—Baidyanath Mukhopadhyay 307

Thiophene :— ... (See Raman Effect)

Thymol :— ... (See Raman Effect)

Titanium Tetrachloride :— (See Magnetism)

Virial Coefficient of Gases :— ... Calculation of the Second—T. S. Wheeler 595

Viscosity :— ... A Note on the Coefficient of, of Liquid Sodium Amalgams—G. R. Paranjpe 95

X-rays :— ... X-ray Analysis of the Structure of Diphenyl—Jagattaran Dhar ... 43

Surface Convection and Variation of Temperature near a Hot Surface

By

L. A. Ramdas and S. L. Malurkar.

(Plates I, II and III.)

(*Received for publication, 2nd January, 1932.*)

Abstract.

The paper is in continuation of the previous communication entitled "Theory of extremely high lapse-rates of temperature very near the ground." In Part I the nature of the turbulence near a hot surface is experimentally shown to consist of the upward incursions of very hot (dust-free) air near the plate and the downward movement of the colder air above. These movements are also suitably illustrated.

In Part II laboratory measurements of temperature above and below a hot plate are discussed. The variation of temperature with height both in the skin layer and in the surface layer agrees more or less with the theoretical expression derived in our previous paper.

The value of α in the surface layer is about 0·29 ; this is found to be 15 times that in the skin layer in the same experiments.

There also appears to be a "boundary layer" of the order of 1 mm. or so in thickness in which extremely low heat conductivity probably prevails. It is hoped to extend the temperature measurements into this layer to verify this point.

Introduction.

In a recent paper it has been shown that the temperature distribution very near the ground on a clear day under the steady conditions prevailing at the time of the diurnal maximum temperature can be represented by

$$\phi = \phi_0 \frac{\sinh a(h-z)}{\sinh ah}$$

where ϕ is the variable part of temperature, ϕ_0 is a constant, and h is the thickness of the "surface layer"; a is a constant equal to $\sqrt{\frac{16a\sigma\theta_0{}^3}{k}}$ involving the effective absorption co-efficient a of water vapour per centimetre and σ the Stefan Boltzman's constant; θ_0 is the absolute temperature, and k is the conductivity term due to convection processes.

In the present paper we confine ourselves to a discussion of results obtained from laboratory experiments. In Part I the nature of the convection process prevailing very near a hot surface will be discussed. In Part II it will be shown that the observed distribution of temperature near a hot surface is in fair agreement with the theory proposed by us in the earlier paper.

Further applications of the theory to actual meteorological conditions will be considered in a later paper.

PART I.

The mechanism of the conduction of heat upwards from a hot surface by means of surface turbulence.

The mechanism responsible for conveying heat upwards from a horizontal hot surface exposed to the atmosphere is not well understood at present. From observations on "shimmering" on a hot day one may conclude that there must be an interchange of hot air tending to ascend and cold air tending to descend. In a previous note this state of affairs was represented roughly by arrows pointing upwards to show hot ascending air and arrows pointing downwards to show the cold descending air.

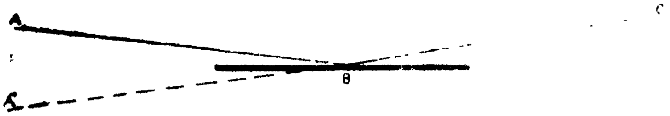

FIG. 1.

A number of experiments were made in the laboratory to discover the actual phenomena involved in such a process. A plane sheet of iron B (see Figure 1), $1\frac{1}{2}$ ft. by $4\frac{1}{2}$ ft. was heated from below. As soon as the plate began to get hot shimmering was visible. A long glass tube A the lower surface of which provided a bright linear source of light when exposed to the sky-light near a window at a distance of 15 feet from the hot plate, was kept horizontal and adjusted so as to be very slightly above the upper surface of the hot plate. On viewing the illuminated lower surface of the glass tube from C in a direction almost parallel to the hot surface its mirage image could be seen distinctly. On carefully watching the reflected image it was found that the image A′ was wavy in form, the number of crests being more or less the same from time to time. Ordinarily, whenever there was the slightest movement of air across the space above the hot plate, a train of waves passed along the mirage image in the direction of the draught, but the cessation of any general drift of air did not cause the image to become straight. This shows that the waviness of the image is independent of any outside agency and that as long as the plate is hot the surface convection responsible for it will continue. The appearance of the straight object and its wavy mirage image is shown by the figures in Plate I which are photographs taken with a camera provided with telephoto attachment with exposures of the order of $\frac{1}{10}$ second. It may be noted that the undulations of the image correspond to simultaneous undulations of an equivalent plane which may be considered to be responsible for the mirage reflection. The size of an undulation above the plate is about 2 cms. It is clear that the deformation of the equivalent reflecting plane (which is a millimetre or so above the actual heated surface) must be due to some type of convection in which the heated air tries to break through colder layers above and the latter tries to take its place so as to complete the local circulation. In this connection it will be interesting to see the figures in Plate II which represent the steam figures obtained by spreading a thin layer of water on the hot plate. These discontinuous isolated columns in which the steam rises are indeed very suggestive.

An interesting observation was made while watching the steam figures. It was noticed that below the steam, and in contact with the hot surface was a dark space about 1 or 2 mms. thick which was free from steam and which persisted under all circumstances ; the upper boundary of this layer underwent fluctuations similar to those indicated by the mirage image (see Plate I). This observation together with the extraordinarily rapid fall of temperature noticed in the first few mms. above a hot surface suggested that one has to deal with fluctuations in the dark space observed in the steam experiment.

Our attention was drawn at this stage to the work of Tyndall,[1] Rayleigh,[2] Aitken,[3] Lodge [4] and Clark done between 1870 and 1885 on the region of warm dust-free air around hot bodies. Aitken performed numerous interesting experiments bringing out the essential features of this phenomenon. The

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[1] Tyndall, Proc. Roy. Inst., London, **6**, 1 (1870).

[2] Rayleigh, Proc. Roy. Soc., Dec. (1882).

[3] Aitken, "On the formation of small clear spaces in dusty air," Trans. Roy. Soc., Edinburgh, **32**, 239-272 (1884).

[4] O. J. Lodge and J. W. Clark, "On the phenomena exhibited by dusty air in the neighbourhood of strongly illuminated bodies, Proc. Phy. Soc., London, **6**, 1-29 (1884). Also Phil. Mag., **17**, 214 239 (1884). See also a recent note by W. J. Hooper on "the deposition of dust on walls," Physics, Vol. 1, No. 1, 1931 (July).

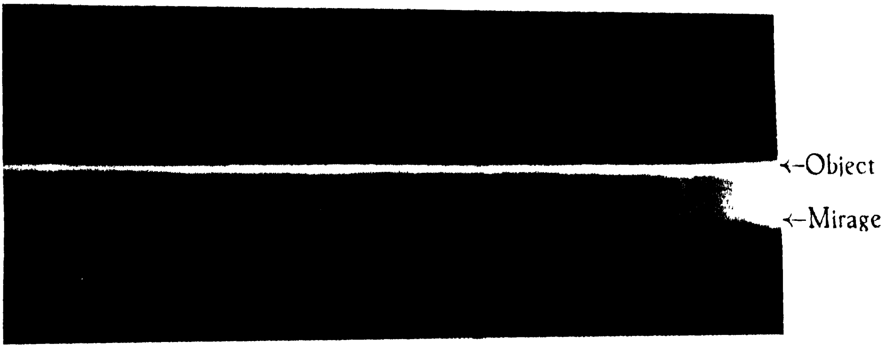

Fig. 1.

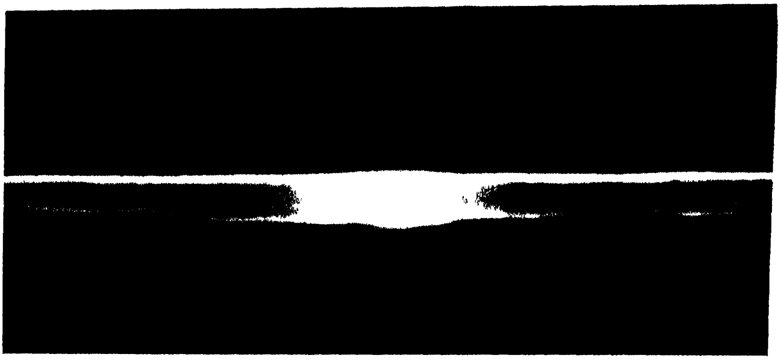

Fig. 2.

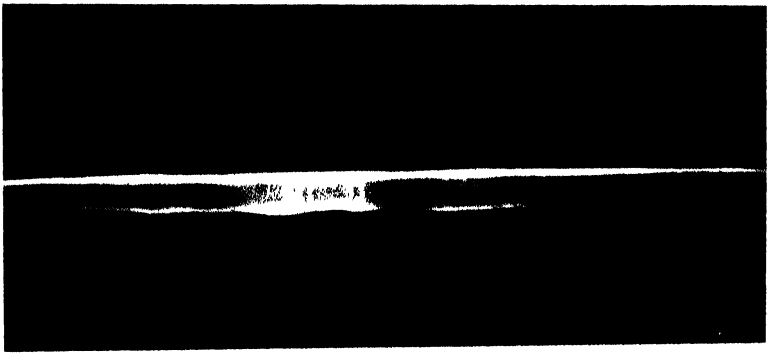

Fig. 3.

Fluctuations of the mirage reflecting plane over a hot plate.

general explanation of the phenomenon was given by Lodge. Briefly, the explanation is that owing to the very large temperature gradient near a hot body a dust particle receives less momentum by molecular bombardment on the side away from a horizontal hot surface than on the side facing it. This differential bombardment by molecules connotes a slight difference of pressure which ought to vanish in the steady state (*i.e.*, steady from a molecular standpoint where only molecular diffusion prevails). In all these experiments, however, a steady state is never reached as there is a continuous convection set up near the hot surface where fresh air is being continuously brought by the convection process and made warmer.

The explanation given by Lodge is qualitative. The whole phenomenon is being critically examined both experimentally and theoretically in order to see (1) whether it is molecular in origin and (2) whether there are any points of similarity to the "boundary layer" which is known to exist when a current of air is flowing past a solid surface.

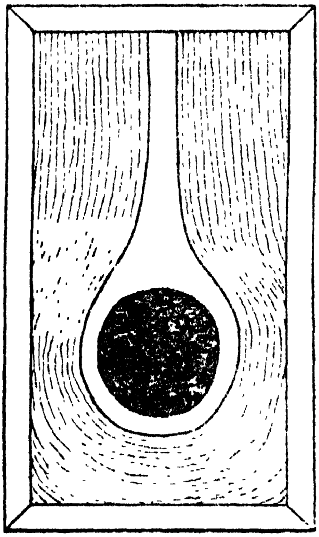

FIG. 2(*a*).

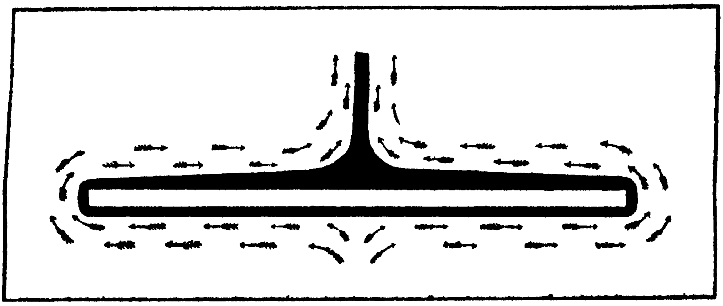

FIG. 2(*b*).

Fig. 2 (*a*) shows the appearance of the thin dust-free layer surrounding a hot sphere immersed in a dusty atmosphere. Fig. 2(*b*) shows what happens when a small heated plate is similarly exposed. These are reproduced here from the original figures given by Aitken. It may be noticed that in both cases the dust-free air ascends above the centre of the heated object like a wedge. Most of the previous workers seem to have used hot objects which had areas of the order of 2 or 3 centimetres square enclosed in observation chambers of small dimensions, as their object was to see the dark space in a steady or undisturbed state and to explain its origin. But very interesting results are obtained when the dimensions of the hot plate and its enclosure are of sufficiently large magnitude. Smoke from burning sulphur and ammonium chloride fumes are found suitable for making these phenomena visible. When the hot plate rests over an extensive surface to cut off the influence of the under side, the situation is no longer that suggested by Fig. 2(*b*). On illuminating the cloud of ammonium chloride or sulphur smoke by means of a condensed beam of sunlight, one begins to see that the dust-free hot air near the plate actually shoots up into not one, but several tongues of ascending air; these dark columns of hot air rushing up into the cold air above, extend several centimetres upwards, but while their base near the hot surface is 1½ to 2½ cms. broad, their width rapidly diminishes towards the apex.

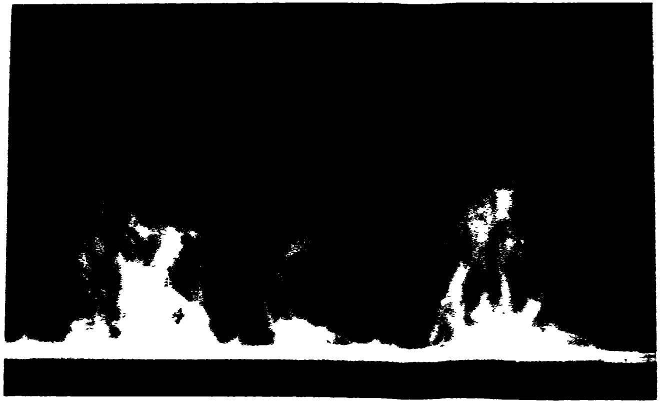

Fig. 1.

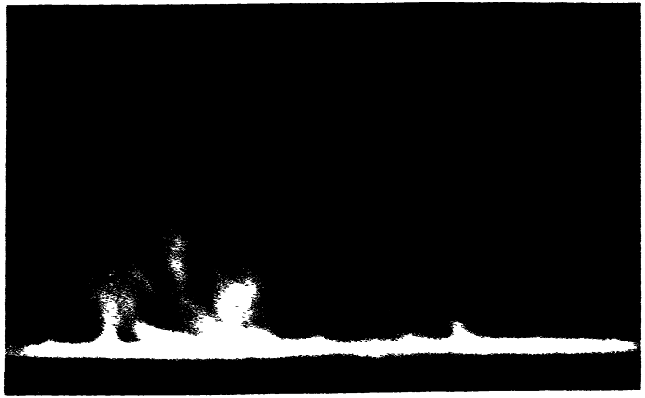

Fig. 2

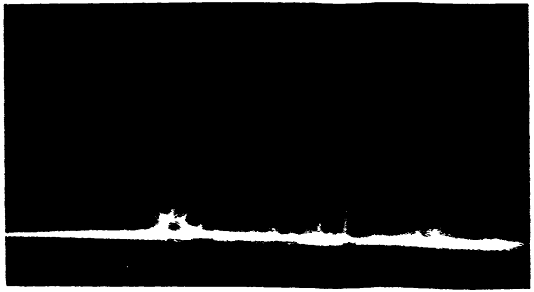

Fig. 3.

Fig. 4.

Stream figures over heated plate

These dark columns are by no means stationary as in the experiments of Aitken or Lodge ; they develop and move about in a random manner with a tendency to drift with a general wind, if any, across the plate. The corresponding downward movements by the side of these hot ascending columns are not very distinct if the plate is large and there are numerous ascending columns ; if the experiment is repeated on a smaller scale it can be seen that, while the hot wedge thrusts itself upwards, two vortices also appear one on either side ; the direction of motion of these vortices is roughly as shown in Figure 3. It may be seen that while the motion in the smoky vortex is in the same direction as the ascending dust-free column of hot air adjacent to it, away from it the motion is downward. The detailed structure of the ascending and descending columns under controlled conditions is under investigation, but for our present purpose it is sufficient to note that the process responsible for the supply of heat from the hot surface to the upper layers is the ascent of the dust-free columns which are at any instant distributed above the plate in a more or less irregular pattern ; every ascent inducing or being accompanied by a descent of the colder air. The figures in plate III show a side view of this phenomenon. The photographs were taken with Gavart plates (speed 700) using sunlight for illumination with exposures of $\frac{1}{10}$ of a second.

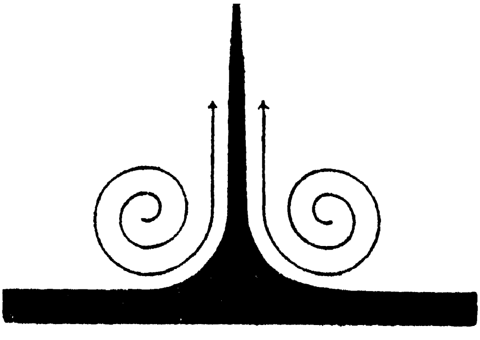

FIG. 3.

The upward velocity in the ascending columns is found to be small near the surface, but rapidly increases a few centimetres above the plate. This was also observed in the steam figure experiments. On occasions when the up-streaming was sufficiently vigorous, one could even observe a series of vortices one above the other generated by the column on either side of it during its vigorous ascent.

One can easily visualise now what caused the undulations in the mirage reflection referred to previously and the shimmering round hot bodies. The fundamental nature of the skin layer cannot be over-emphasized in all these cases where instability between a heated layer below and a colder layer above is the cause of the observed phenomena.

It may be mentioned here that, when a vessel containing hot water is placed in the observation chamber, the skin layer and ascending columns of warm moist air are easily seen. There seems to be no essential difference from the phenomenon above a hot solid plate except that the ascending tongues convey not only heat but also moisture upwards. The variation of temperature and humidity over a surface of water is of great meteorological interest. The problem is therefore now under detailed investigation.

Phenomena below the heated plate.

We have so far confined our attention to the phenomena taking place *above* the hot surface. One cannot close this discussion without referring to what takes place *below* the heated plate, when the latter rests over suitable supports so as to expose the bottom surface to the air below. Here also the superheated dust-free layer of air is developed but, as there is no colder air mass above it, all that happens is a slow drifting of the hot air clinging to the underside of the plate as observed by Aitken (see Figure 2 *b*). There is practically no turbulence and the mirage image has no apparent

Fig. 1.

Fig. 2.

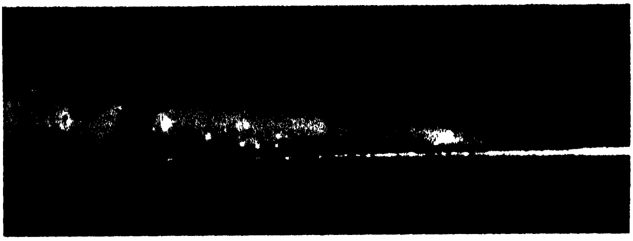

Fig. 3.

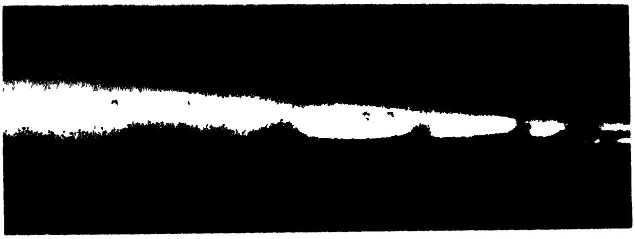

Fig. 4.

Dark space over hot plate and its incursions into the air above.

undulations as in Plate I. The dust-free air turns round the edges and later augments the supply of the superheated air above the upper side of the hot plate ; but, as shown by Aitken and others, the dust-free layer is itself not all manufactured at the bottom of the plate.

That the turbulent convection below a hot plate is very small or negligible is in a way well known ; for this is kept in view in all experiments on molecular heat conductivity of gases.

Questions relating to the discontinuous changes of conductivity while passing from the skin layer just above the hot surface to the "surface layer" which extends higher up to 20 or 30 cms. will be considered in the next part.

PART II.

Temperature distribution near a heated surface.

In this section we shall discuss the distribution of temperature in (1) the surface layer extending from about 1 cm. to 20 or 30 cms. above a hot surface, (2) the skin layer extending up to about 10 mms. above a hot surface and (3) the distribution of temperature in the stable and comparatively turbulence free layer below a hot surface.

Experimental arrangements.

These experiments were made above and below a steam-heated chamber 2 ft. square and 1″ thick made of galvanised iron and provided with suitable inlet and outlet tubes. The source of the steam with its heating arrangements was kept at a sufficient distance so as not to influence the temperature of the air near the experimental chamber ; all radiation from the fire above which the source of steam was kept, was cut off by suitable screens. Two series of measurements were made; in the first series thermometers (Assmann spare thermometers) with the bulbs covered with a highly reflecting metal-foil so as to avoid heating by direct radiation from the hot chamber were used. In the latter series radiation-proof (*i.e.*, silver coated) copper constantine thermal junctions of very small size (about 1 mm. in size) were used, with one of the junctions kept at 60°C. and the other junction at various heights above or below the experimental chamber. To give the temperature readings a calibrated unipivot galvanometer was kept in the circuit. It was found that the results obtained by the two methods gave more or less concordant results. In the first series, owing to the larger size of the thermometer bulbs the skin layer could not be investigated.

Observations in the surface layer.

Fig. 4 shows the distribution of temperature in the surface layer. The crosses are the observed values and circles the theoretical values calculated from the expression

$$\theta=\theta_0+\phi_0\frac{Sinh\ a\ (h-z)}{Sinh\ ah}.$$

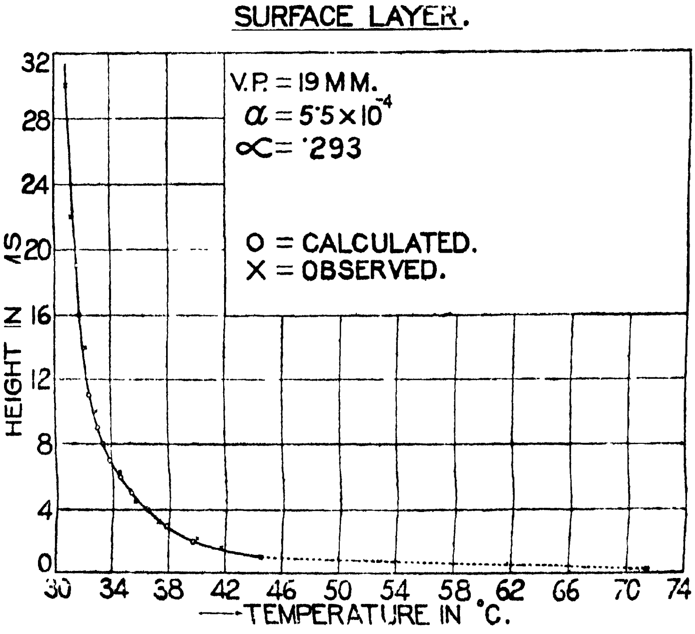

FIG. 4.

It may be noted that the value of a is found to be ·29. Several series of observations confirm these values.

It is interesting to compare these results with those obtained above the road. In this case a was ·26.

It was thought that variations in the temperature distribution arising from variations in the water vapour content from day to day could be determined from the laboratory experiments. Unfortunately the observed variation of the water vapour content as well as of the temperature distribution were too small to be detected. For example the largest variation of the water vapour pressure was from 10 mm. up to 30 mm. From

$$\bar{a} = \sqrt{16\, a\sigma\theta_0^3}$$

it will be seen that we are dealing with the square root of the effective absorption co-efficient of water vapour for long waves. It is hoped to study the influence of a by further experiments inside chambers where the humidity can be altered at will by larger amounts than is possible in the open.

Observations in the skin layer.

Fig. 5 shows the distribution of temperature in the skin layer. Here the heights are given in cms. It will be noticed from the more microscopic standpoint adopted in this figure, that the height-temperature curve has an appearance somewhat similar to the corresponding curve for the surface layer.

2

Magnetic Rotations of Liquid Mixtures

By

RAM NARAIN MATHUR AND AMAR NATH KAPUR.

(Received for publication, 14th January, 1932.)

The magnetic rotation of mixtures of organic liquids, like their diamagnetic susceptibility, is well known to follow an additive law. Recently however the diamagnetism of some mixtures of organic liquids has been found by Trew and Spencer[1] to be considerably different from that calculated from the proportions of the components. Some of the mixtures of diamagnetic liquids have even been found to become paramagnetic. For example, in the case of 50 moles per cent. mixture of acetone and chloroform it is considered that a paramagnetic co-ordination compound with one molecule of acetone and one molecule of chloroform is formed. The magnetic rotation of this mixture should therefore be considerably different from that calculated from the proportions of the components, especially in view of the recent work of Ladenburg,[2] Roberts,[3] etc., who have shown that there are two types of magnetic rotation, the usual diamagnetic rotation and a paramagnetic rotation which arises from paramagnetic atoms.

The magnetic rotations for mixtures of acetone and chloroform have therefore been carefully investigated. Mixtures of ether and chloroform, and ether and acetone have also been investigated to verify the results of Trew and Spencer.

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[1] Proc. Roy. Soc., 131, 209 (1931).

[2] Zeit. f. Physik. xxxiv, p. 898, 1925.

[3] Phil. Mag., 9, 361 (1930).

Experimental.

There are two methods generally employed for the measurement of magnetic rotation: (1) placing the polarimeter tube directly in between the pole-pieces of an electromagnet, and (2) placing the polarimeter tube inside a solenoid. The latter method has been adopted in this investigation. The solenoid employed was wound over a thin fibre tube. It consisted of 25 layers, each having eighty turns of No. 12 S.W.G. D.C.C. copper wire, and a constant current of 12 amperes was passed in it during the observations. Further as magnetic rotation varies with the temperature, it is necessary for our purpose that the observations should all be made at the same temperature. Hollow copper tubing was therefore wound over the polarimeter tube through which water at a constant temperature was continuously circulated. For a source of monochromatic light of high illumination, a sodium burner has been employed. The results obtained are given below :—

TABLE I.

Chloroform-Acetone.

Volume percentage.		Rotation observed.	Rotation calculated.
Acetone.	Chloroform.		
100	...	4·16	...
80	20	4·49	4·527
60	40	4·91	4·895
40	60	5·24	5·26
20	80	5·57	5·63
...	100	5·998	...

TABLE II.

Ether-Chloroform.

Volume percentage.		Rotation observed.	Rotation calculated.
Chloroform.	Ether.		
100	...	5·998	...
80	20	5·56	5·60
60	40	5·19	5 20
40	60	4·86	4·805
20	80	4·42	4·407
...	100	4·01	...

TABLE III.

Ether-Acetone.

Volume percentage.		Rotation observed.	Rotation calculated.
Ether.	Acetone.		
100	...	4·01	...
80	20	4·01	4·04
60	40	4·07	4·07
40	60	4·11	4·10
20	80	4·13	4·13
...	100	4·16	...

Results.

The results obtained by Trew and Spencer have recently been contradicted by Ranganadham[4] and Buchner[5] who find that the experimentally determined values for the diamagnetism of the mixtures do not differ by more than 1 or 2 per cent. from the calculated values. The results obtained for the magnetic rotations of their liquid mixtures also lead to the same conclusion. The maximum difference between the experimental and calculated values for mixtures of acetone and chloroform is of the order of 1·2 per cent. while in the case of ether and acetone there is practically no difference whatsoever. If, however, as Trew and Spencer think, the formation of a paramagnetic co-ordination compound had taken place in these liquid mixtures, their magnetic rotations would have been considerably different from those calculated by the additive law.

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[4] Nature, 127, 1931, p. 975.
[5] Nature, 128, 1931, p. 301.

The Diamagnetism and Structure of some Compounds of Ethylene, Carbon tetrachloride and Titanium tetrachloride

BY

V. I. VAIDHIANATHAN AND BALWANT SINGH.

(*Received for publication, 18th January, 1932.*)

ABSTRACT.

The magnetic susceptibilities of C_2H_4, $C_2H_4(OH)_2$, $C_2H_4(NH_2)_2$, $C_2H_4Cl_2$, $C_2H_4Br_2$, $C_2H_4I_2$, CCl_4 and $TiCl_4$ have been determined, special care being taken to purify the substances by repeated distillations at their boiling points and recrystallisations in the case of $C_2H_4I_2$. A high sensitivity Curie balance with quartz suspension and retorsion head was employed. Deviations from additivity relations were found in most cases. An attempt is made to interpret these deviations from the standpoint of the nature of the valency links.

Introduction.

It is a well-known fact that in organic compounds the molecular susceptibility can be expressed as the sum of the susceptibilities of the atoms composing the molecule. This additive relation holds good in the saturated hydrocarbons fairly accurately, but in the unsaturated hydrocarbons, as also in compounds containing other atoms, there are considerable deviations from the law, the deviation in the latter compounds depending on the nature of the group attached to the carbon atom. Additivity relations also hold good in many diamagnetic inorganic compounds, the molecular susceptibility being equal to the sum of the susceptibilities of the constituent ions. Most of the data for organic compounds on which discussions on additive relations are based are due to Pascal and they are on liquids. Recent measurements have in some cases superseded those of Pascal. It was, therefore, thought worthwhile to systematically examine a few compounds accurately and determine the deviations from additivity when different groups are attached to the carbon atom.

Experimental.

In a previous investigation the value for ethylene has been determined.[1] In the present investigation five compounds of ethylene were selected, *viz.*, glycol, ethylene diamine, ethylene chloride, ethylene bromide and ethylene iodide. To examine fully the effect of the addition of chlorine, carbon tetrachloride and titanium tetrachloride were also examined. Glycol, diamine, ethylene chloride and carbon tetrachloride were Kahlbaum's specimens, but were distilled two or three times. The susceptibility was determined after each purification. The bromide and iodide were prepared in the laboratory. The iodide was recrystallised until its boiling point was constant and the susceptibility was determined after each purification. Titanium tetrachloride was Merck's extra pure specimen, but could not be further chemically purified due to its highly fuming nature. An analysis of the specimen was made subsequently but was not found to contain any appreciable impurity especially of iron or other ferromagnetic compounds which are liable to introduce errors.

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[1] The value of C_2H_4 is taken from a previous paper by V. I. Vaidhianathan, Ind. Jour. Phys., **3**, 165 (1928). In a subsequent investigation F. Bitter in Physical Review, **33**, 389 (1929), obtains a still lower value. The I. C. T. value for specific susceptibility of ethylene is three times the value obtained in these investigations and appears to be wrong.

A high sensitivity Curie Balance with quartz suspension and retorsion head was employed. The spot of light attached to the beam was brought back to the original position. The retorsion angles were generally about 8 to 10 degrees and they could be read accurate to 2 minutes of arc. The liquids were sealed in very thin pyrex tubes to prevent evaporation and the mean of a number of readings was taken. Correction for the empty capsule was applied. Equal volumes were taken in all cases and the pull against air could be neglected since the values were compared with that of water. The latter value was taken as 0·720.[2] The mean temperature at which the investigations were made, was 32°C., and a field strength of nearly 4000 Gauss was employed. The current in the magnet was kept quite constant with finely adjustable resistances and the readings were quite consistent. The advantage of the torsion method is that it can be made very sensitive and the comparisons can be pushed to the extreme limit of accuracy. The main difficulty is the maintenance of the field and particular care was taken to maintain the field constant. The values are considered accurate to within 0·5 per cent. Possibly in titanium tetrachloride the value is accurate to about 5 per cent. only.

Results.

The values obtained are given in the following table. Column 5 gives theoretical values obtained by the addition of the susceptibilities of the constituent elements. Column 6 gives the difference between the theoretical and the experimental values. In obtaining the additive value for titanium tetrachloride, the value of the Ti^{+4} ion is calculated from the known value of Ca^{+2} ion, for there is no experimental determination of the former. The value thus obtained is -13.2.

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[2] The values given in the paper are in units of 10^{-6}.

TABLE I.

Substance.	Formula.	Sp. χ	Mol. χ	Additive value.	Difference.
Ethylene (gas)	C_2H_4	0·546	15·30	23·80	+8·5
Glycol	$C_2H_4(OH)_2$	0·638	39·58	38·9	−0·68
Ethylene diamine	$C_2H_4(NH)_2$	0·771	46·26	45·8	−0·46
Ethylene chloride	$C_2H_4Cl_2$	0·602	59·62	68·3	+8·68
Ethylene bromide	$C_2H_4Br_2$	0·412	77·37	88·44	+11·07
Ethylene iodide	$C_2H_4I_2$	0·371	104·7	115·3	+10·6
Carbon tetrachloride	CCl_4	0·427$_9$	65·7	83·2	+17·5
Titanium tetrachloride	$TiCl_4$	0·287	54·54	93·6	+39·1

In obtaining the additive value, the following diamagnetic values are taken for the constituent elements or ions composing the molecule. C = 6, H = 2·95, N = 5·1, Cl = 20·1 Br = 30·6, I = 44·6, O = 4·4, Ti = 13·2. The last column indicates the value to be added to the experimental value to obtain the additive value.

Discussion.

In the case of ethylene the decrease of diamagnetism due to the double bond is interpreted as due to the concentration of the positive nuclei of the two carbon atoms, which as a consequence behave as though they form a single centre of force for the outer electrons which are magnetically important.[3] The fact that sulphur and ethylene have the same susceptibility and the same number of electrons lend support to the possibility of such an electron configuration.[4]

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[3] Stoner, Magnetism and Atomic Structure, p. 332, 1926.

[4] The question of ethylene has been considered in a previous paper, Vaidhianathan, *loc. cit.* The decrease of diamagnetism due to the double bond C = C is 5·5 as deduced by Pascal from measurements in the liquid state. As deduced from the ethylene gas this decrease is 8·5.

It was the object of the present investigation to see if some quantitative relation could be found between the deviations from additivity and the nature of the valency links. Though quantitative relations could not be arrived at, qualitatively it appears that a satisfactory interpretation could be obtained by considering the different kinds of valence links and their effects on the diamagnetism of the molecule.

For example, in the case of a polar molecule like KCl the value of diamagnetism obtained is equal to the sum of the values for Cl and K ions. The value for KCl, whether it is deduced from solution or is determined from the solid state is the same. In solution the ions are free and have a distinct existence. The fact that in the solid form the diamagnetic value does not differ from that in the solution points to the existence of the free ions in the solid, which are held by the electrostatic attraction in the crystal lattice. K^+ and Cl^- have both an argon configuration, the former being positively charged and the latter negatively. The value theoretically deduced is also equal to the experimental. In the case of many simple polar compounds, such relations are found to hold good.

Taking the case of a molecule of carbon tetrachloride or ethylene chloride, what is the nature of the valency link best in accord with their diamagnetic property ?[5] It is observed that when a chlorine atom is linked with a carbon atom in ethylene chloride or carbon tetrachloride, a decrease in diamagnetism results. This is found to be 4·34 in the former and 4·37 in the latter for each C-Cl link. The equal decrease is possibly in the nature of the C-Cl links in both the molecules.

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[5] For the different kinds of valency links according to chemical evidence, see Sidgwick, Electronic Theory of Valency, p. 58 (1927).

According to Kossel,[6] a CCl_4 molecule is representedas possessing a central carbon atom which has lost by transfer 4 electrons, each of the chlorines having taken up one and completed its argon configuration. The central C atom has now the helium structure. The atoms are held by electrostatic attraction. The diamagnetic susceptibility according to such configuration can be computed. By comparison with the susceptibility of helium it can be shown that the C atom in CCl_4 should contribute 0·3 to the susceptibility of the molecule. For, the larger nuclear charge in C contracts the K orbit which has the same configuration as helium, and for similar configurations the susceptibilities are proportional to the areas of the orbit, which again are inversely as the square of the nuclear charge. For chlorine the value deduced from the various compounds and ions is 20·1. Hence the total mol. susceptibility of CCl_4 should be 5·7 less than the value obtained by treating the atoms as non-ionised. The observed value however is still smaller than this.

A second kind of valence link according to chemical evidence is the shared one, where the valency electron is common to both the nuclei. The simplest type of such an orbit is an elliptical one where the valency electron moves round encircling both the nuclei. This is the covalent link as distinct from an electrovalent one considered in the previous paragraph. In the case of such a single orbit existing in the C-Cl link its contribution might be paramagnetic, and the observed numerical diminutino in diamagnetic susceptibility might thus be explained.

A very interesting case is that of $TiCl_4$. This compound does not seem to have been investigated before. Ti and its compounds so far investigated are paramagnetic (I.C.T.). But $TiCl_4$ is diamagnetic as might be expected. Qualitatively the idea that four electrons are transferred from the central titanium atom to each of the chlorines, each having the argon configuration is in agreement with its diamagnetism. The central titanium atom when it has given up four electrons has 18 electrons left, so that each Ti-Cl link presents a problem analogous to the K-Cl link. The additive value for the molecule should be 93·6 whereas the observed value is 54·5, which is 80% smaller. On the other hand, using the idea of shared orbits as in CCl_4, the decrease is intelligible. The decrease, however, is about twice that in CCl_4, approximately 9·79 per Ti-Cl link. In connection with the covalent linkage between Ti and Cl atoms suggested above, it is to be noted that titanium chloride is not ionisable as the corresponding halides of calcium or potassium, but hydrolyses considerably.

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[6] For a diagrammatic representation of the CCl_4 molecule according to Kossel, see Bragg's X-Ray and Crystal Structure, p. 158 (1927).

In the case of glycol the additivity law is obeyed, but an arbitrary value—4·4 is to be imposed on the oxygen to obtain agreement. Whenever an OH group is attached to the carbon atom, this value of oxygen brings the experimental and theoretical values in agreement. Chemically there is very little significance in imposing this value of oxygen in the alcohols. On the other hand, it is the group OH which has 9 electrons that tends to complete a ten electron system by transfer or sharing. A free OH has a susceptibility—12·6 according to Pauling.[7] As in the case of the chloride, bromide or iodide if we take this ionic value of OH, the theoretical value of glycol should be 9·42 larger than the experimental value. From this standpoint glycol also shows a decrease as the other compounds discussed above do. The compound glycol though polar is non-ionisable. It seems that magnetic considerations do enable non-ionisable and ionisable links to be distinguished when taken in conjunction with other evidences at least in simple cases.

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[7] L. Pauling, Proc. Roy. Soc., A 114, 181 (1927).

In the case of ethylene diamine theobserved value is nearly equal to the additive one, when a value −5·1 is given to nitrogen. There is no experimental or theoretical value for the free amine ion in solution or ionisable compounds to see if this compound behaves differently from others. Since there are three nuclei in the amine group, it is probable that when attached to the C atom the electrons move about the different centres of force and in that case the diamagnetism cannot be expected to show a decrease. It is worthy of note that though the OH and the NH_2 have both 9 electrons, the former has a considerably larger scattering power for X-rays than the latter and this indicates a concentration of the electronic charge in the former. A larger diamagnetism than in OH may therefore be expected in the NH_2 group.

It has been possible in this paper to consider only some typical simple compounds from the standpoint of the two kinds of valency links. There are possibly links which are intermediate between the electrovalent (electron transfer) and the covalent (electron sharing) links. Summarising, it may be said that the examination of the accurate data of the diamagnetism of compounds seems to be fruitful for deciding their electronic structure.

We have great pleasure in thanking the Punjab Chemical Research Fund Committee, for the grant of a scholarship to the junior author for carrying on these investigations.

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4

On the " Performance Test " in Statistics

By

S. R. Savur

(*Received for publication, 29th January, 1932*)

In a recent issue[1] * of the Quarterly Journal of the Royal Meteorological Society, Dr. C. W. B. Normand has mentioned a valuable test which he has named the "Performance test." This test has been stated incidentally among a host of other things so that there is a possibility of its being overlooked. Besides, the different uses to which this test could be put have not been discussed there. In this short preliminary note, therefore, some applications of this important test will be given.

As this test was first stressed in connection with finding the significance of correlation co-efficients or regression formulae, we shall begin with its applications to these cases. It may be wondered whether there is any need for a new test when already there appear to be a large number for such a purpose. We have, in the first place, Pearson and Filon's formula[2] for the probable error of a simple correlation co-efficient when the number of observations is not small. Then there is Walker's addition[3] to it. More accurate tests depending on Fisher's investigation[4] can be made using the tables given in the joint paper by Soper, Young, Cave, Lee and Pearson.[5] A variety of such tests, from a practical point of view, will be found in Fisher's admirable book "Statistical Methods for Research Workers" or in Ezekiel's valuable book.* In spite of the number of these tests the need for a test, such as that suggested by Dr. Normand, can be seen from the following considerations.

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* The references are given at the end of the paper.

Suppose we wish to find a formula for forecasting rain at a particular place. We correlate the rainfall at that place with a number of other factors. We choose, say, four or five of these factors to form a multiple regression equation. In choosing these factors we do not merely consider the large magnitude of their correlation co-efficients with our rainfall, but we also see that the intercorrelations between these factors are small. The selection is not only thus complicated but is mainly individual in that different persons are likely to choose diverse factors from the same lot. Now no test has yet been devised to take an adequate account of these individual vagaries. It is in such cases that Dr. Normand's test is particularly valuable.

Because of the almost insuperable theoretical difficulties in the way of devising a suitable test in which the individual judgments have been allowed for, the performance test is based upon the behaviour of the formula *subsequent* to the date up to which the data have been used in computing that formula. That is to say, using the above illustration, suppose data up to the end of 1931 have been used to calculate the best multiple regression formula for the annual rainfall. To find the true C.C. of this formula, Dr. Normand suggests waiting for a few years, say 20 or 25 years at least, so as to minimise the probable error, and then finding the C.C. between the actual rainfall and that calculated from this formula *after*

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* Methods of Correlation Analysis, by Mordecai Ezekiel, published by John Wiley & Sons, Inc., New York, 1930

1931. *To this C.C. can be applied the usual tests of significance for a random simple C.C. and we can thus obtain the probable value of the true C.C. of the formula.* The nearer this C.C. is to that of the formula prior to its testing, the nearer will it be to the true value of the C.C. We have thus got a test in which individual bias has been completely eliminated. This is the performance test and herein lies its value, its simplicity and beauty.

This test is so obvious, once it is pointed out, that it is surprising that it has not been emphasised before. To a modified extent it has been used by Sir G. T. Walker[17] to test his 1908 formula for forecasting monsoon rainfall in India and by Dinsmore Alter[6] for a similar purpose in connection with his formula for forecasting British rainfall. Both were, however, mainly concerned to point out that the C.Cs. *subsequent* to the date on which the formulae were computed were still high. Neither of them calculated the errors to which these C.C.s are subject, or appear to have suggested that the test could be used in the way pointed out by Dr. Normand.

A Few Applications of the Test.

(1) *Multiple correlation formulae.*—For forecasting various seasonal rainfalls in India G. T. Walker devised six forecasting formulae.[7] Although some of these were computed as early as 1920, they were all published in 1924 in the Memoir[7] referred to above. We shall call these the "1924 formulae." Recently[8] they were recalculated using data up to the end of 1929 or 1930. These new formulae will be termed the "1930 formulae." The 1924 formulae are therefore suitable for the application of Dr. Normand's test, but the periods, ranging from 11 to 8 years, are rather small. The results are shown in the table below.

TABLE I.

Correlation Co-efficient.

Forecasted element.	1924 formula.	1930 formula.	From Dr. Normand's test	
A North-west India winter precipitation.	+ 0·76	+ 0·54	−·07	±·23
A Peninsula June-Sept. rainfall.	0·76	0·69	+·14	±·26
C N. W. India do. do.	0·76	0·64	−·20	±·24
D N. E. India do. do.	0·52	0·39	−·06	±·25
E Peninsula Aug.-Sept. rainfall.	0·66	0·64	+·63	±·13
F N. W. India do. do.	0·70	0·61	+·18	±·20

The co-efficients from Dr. Normand's performance test have all very large probable errors (excepting for the formula E) due to the smallness of the C.Cs. and of the periods. Hence no definite conclusions can be drawn in these cases. But we may with great confidence say that formula E is the best of the lot and that the real value of its C.C. is likely to lie within the limits mentioned above. A different analysis made on the assumption that the factors were chosen at random,[8] placed B first and E second in the decreasing order of significance. In view of the above, however, E has to be placed first. The relative order of the remaining cannot be definitely decided until a few more years elapse. The above analysis has been given mainly as an example of the practical application of Dr. Normand's test to multiple regression formulae.

(2) *Simple correlation coefficients.*—When we work out a number of simple C.Cs. we apply Walker's test [3] to find out which of them are significant. According to the performance

test we must exclude from Walker's test those factors which have been selected on other grounds, and in these cases the C.Cs- must be worked out using data *subsequent* to the date on which they have been first selected, applying to each of theses C.Cs. the usual formula for a simple C.C. to find out its probable error. Examples of such cases have already been given by Dr. Normand.[1] We will select only two out of them.

Snowfall accumulation on the Himalayas to the end of May was found more than 50 years back to affect adversely the monsoon rains in India, especially in North-West India. Normand's test gives us the C.C. between the Himalayan snowfall and North-Western India rain (June-Sept.) as—0·31 ±·09.

Again the Lockyers noted the inverse relationship between South American pressure and Indian pressure early this century. This suggested a relationship between the former and the rainfall in India. The co-efficients obtained as above are—

	C.C. by Dr. Normand's test.	
S. Amer. pressure-Peninsula rain (June-Sept.) ...	+0·34	±·12
S. Amer. pressure-N. W. India rain (June-Sept.) ...	+0·53	±·12

We may therefore conclude that the values to which these co-efficients will tend after many years are likely to be within the respective limits mentioned above.

A better approximation to the true C.C. may be obtained by the application of Fishers' principle of "Maximum likelihood." Details will be given in a fuller paper which is under preparation.

(3) *Selection of factors for a forecasting formula.*—For a large number of meteorological elements reliable data are available at present for not less than 60 years. Suppose

we wish to find a formula for forecasting or, as Walker[9] has suggested, for foreshadowing rainfall at some particular place. Let there be a number of factors to choose from for which data are available, say from 1871-1930, *i.e.*, for 60 years. We correlate the rainfall with the various factors using the data for the 1st half period only, *i.e.*, from 1871-1900 and selecting the best we compute a multiple regression formula. Using this formula we calculate the rainfall for the second half of the period and correlate the calculated values with the actual. In whatever way our choice may have been made, this C.C. will give the probable value of the true C.C. of the formula within the usual limits of error found in the manner suggested in a previous paragraph. We will therefore be in a much better position to know the confidence that can be placed in the forecasts from this formula. If this C.C. is positive and is considered to be sufficiently big * we may use the full data for getting a more accurate formula ; if not, fresh factors will have to be looked for.

(4) *Realities of periodicities.*—It is interesting to note that a test intended for finding the significance of correlation co-efficients can be extended to a different sphere altogether. This proves that the test is quite general.

When we analyse a set of data for periodicities, we may apply Schuster's criterion[10] as extended and used by Walker[8] and[11] to discover the reality of the periods found by us. In spite of this it is not a little disconcerting to find that the same set of data when analysed by different investigators have not always yielded similar results. Analysing sunspots Schuster[12] found three periods, *viz.*, 11·125, 8·36 and 4·80 years. Larmor and Yamaga[13] doubted the existence of the 8·36 year period. Turner[14] found that the first period suggested by Schuster was more nearly 11·5 years. Michelson[15] who analysed these data by a harmonic analyser concluded that there were no noteworthy periods at all! In view of these conflicting deductions, it is not a little consoling to think that a natural extension of the general principle involved in Dr. Normand's performance test will give us a test for finding the reality of periods.

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* Some forecasters are satisfied with values of C.C. as low as 0·5 while others want values not less than 0·71 ($= \sqrt{0·5}$).

The extension is simply the following. We divide the data into two halves and analyse each half separately for periodicities. If there are any common periods these are real, if none we may reasonably conclude there are no significant periods.

It is true that a similar process has been tried before,[1] but there the periods had been divided into more than two portions and had some common intervals. The point that is especially stressed upon now is that the whole data should be divided into two portions, preferably equal as may be inferred from the analysis given before[16] with no *overlapping* periods at all. These two are quite essential for the application of the test.

This test was applied to the rainfall at Madras for which there is an unbroken record since 1813. The annual rainfall data were divided into two halves of 59 years each and were analysed for periodicities by a simplified method suggested by the author.[16] The first half gave the periods of 9·12 and 16 years, while the second half yielded the periods of 5, 7, 12 and 14½ years. It is easy to see that the most important and real period is 12 years. To see whether there are minor real periods this period of 12 years should be eliminated from the original data as suggested by Turner,[14] and the residuals analysed for such periodicities in the above manner. This work is in progress.

In conclusion it is hoped that in addition to the above-mentioned uses to which Dr. Normand's performance test can be put, many others will be discovered for this general and very valuable test. A paper in which the applications of this test are given in greater detail is in progress.

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[3] G. T. Walker : Mem. Ind. Meteorolog. Deptt., 21, 1914, pp. 13-15.

[4] R. A. Fisher : Biom., 10, pp. 507-521.

[5] H. E. Soper, A. W. Young, B. M. Cave, A. Lee and K. Pearson : Biom. 11, pp. 328-418.

[6] Dinsmore Alter : Q.J.R. Meteorolog. Soc., 57, 1931, pp. 198-200.

[7] G. T. Walker ; Mem. Ind. Meteorolog. Deptt., 21, 1924, pp. 333-345.

[8] S. R. Savur ; Ind. Meteorolog. Deptt., Sc. Notes, IV, No. 37.

[9] G. T. Walker : Q.J.R. Meteorolog. Soc., 56, 1930, pp. 359-362.

[10] A. Schuster : Terrestrial Magnetism, 3, 1898, pp. 13-41.

[11] G. T. Walker: Mem. Roy. Meteorolog. Soc., 3, No. 25, 1930.

[12] A. Schuster ; "Phil. Trans." A, 206, 1906, pp. 69-100.

[13] J. Larmor and Yamaga : Proc. Roy. Soc., A, 93, 1917, pp. 493-506.

[14] H. H. Turner : Month. Not. Roy. Astr. Soc., 73, 1913, pp. 714-732.

[15] A. A. Michelson : Astro. Phy. Journ., 38, 1913, pp. 268-274.

[16] S. R. Savur : Ind. Journ. Phys.

[17] G. T. Walker: Mem. Ind. Meteorolog. Deptt., 23, 1922, pp. 22-39.

5

The Diamagnetism of Bismuth

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ABSTRACT.

Colloidal bismuth when melted and recrystallised shows an increase in its diamagnetic susceptibility value (χ). This result confirms the observation that χ decreases with particle size. Attention is drawn to the work of Goetz who finds that there is a superposition of a macroscopic structure on the lattice structure in bismuth crystals. The possibility of a connection between this mosaic structure and the variation of the diamagnetic susceptibility with particle size is indicated.

1. *Introduction.*

Vaidyanathan[1] showed that when bismuth was mechanically or electrically colloidalized, the value of the diamagnetic susceptibility decreased considerably from the mass value. He also drew attention to similar observations by Honda and Owen.[2] Bhatnagar[3] and later Mathur and Varma[4] concluded as a result of careful experiments that this fall in the susceptibility value might be due to mere oxidation. Their investigations showed that when the oxide-coated colloidal particles were treated with tartaric acid to dissolve the oxide layer, then washed with alcohol, dried and examined, the susceptibility showed a considerable rise in value. The author[5] examined the question carefully with well graded particles and found that even after tartaric acid treatment, χ was much less than the regulus value. It was found also that χ varied as the inverse of the diameter of the particles. Similar observations were made also with graphite.

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[1] Ind. Jour. Phys., 5, 559 (1930).

[2] Ann. der. Phys., 37, 657 (1912).

[3] Ind. Chem. Soc. Jour., 7, 975 (1930).

[4] Ind. Jour. Phys., 6, 181 (1931).

The significance of these observations has been greatly increased by the recent remarkable results of Goetz and Hergenrother[6] who have found that in bismuth crystal, besides the lattice structure, there is also a secondary structure of macroscopic dimensions. The side of the elementary pyramid was found by Goetz[7] to be $1{\cdot}4\mu$. It is a strange coincidence that the diamagnetic susceptibility of bismuth begins to decrease comparatively rapidly at particle sizes less than about $1{\cdot}5\mu$. There seems to be little doubt that the two phenomena are related to each other. This point will be treated at some length later.

In this paper some experiments are described which go to confirm the reality of the effect of decreasing diamagnetic susceptibility with particle size. Instead of the ordinary method of powdering crystalline bismuth, an attempt has been made to re-crystallise the metal powder by melting it in vacuo and slow cooling. If the diamagnetism does not depend on particle size, then on melting and re-crystallising there should be no change in the value of χ. But it is found that there is a rise in its value after heat treatment.

2. *Experiment.*

Bismuth colloidal powders were prepared in the same manner as detailed in paper I. They were carefully washed and then treated with a strong solution of tartaric acid and gently boiled. This was repeated twice or thrice, the solution being thrown off each time. The powder was then washed several times with alcohol and then transferred in the presence of alcohol to glass tubes having small bulbs blown at one end. These tubes were evacuated and sealed when the powders were dry. Similar bulbs were also blown from the same glass tubes and sealed without any powder inside.

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[5] Ind. Jour. Phys., 6, 241 (1931). This paper will hereafter be called paper I.

[6] Phys. Rev., 38, 2075 (1931).

[7] Proc. Nat. Acad. Sci., 16, 99 (1930).

These bulbs containing the powders and the empty ones were now investigated with a Curie balance, the deflection for each bulb being noted. Three benzene bulbs were used as the comparison bulbs, the amounts of benzene being adjusted to give three different ranges of deflection.

The bulbs were now placed inside an electric heater and then heated gradually to a temperature of 275° to 280°, *i.e.*, a few degrees higher than the melting point of bismuth. The bulbs were now allowed to remain at this temperature for nearly two hours and then allowed to cool gradually to the room temperature in the course of 6 to 8 hours. This was done by gradually decreasing the current through the heater.

It was found on examining the metal that it had melted in each bulb and had collected into a mass. All the bulbs were now reinvestigated with the Curie balance and the deflections were corrected with the standard benzene bulbs.

The bulbs were broken open and the bismuth dissolved by nitric acid. They were then cleaned with distilled water and dried in a vacuum desiccator. The deflections of the bulbs alone were then determined.

From these readings it was possible to calculate the diamagnetic susceptibility of the colloidal powder before and after heat treatment. The results with empty bulbs showed no change of deflection arising from the containers after heat treatment. In this method, the effect of any oxide left behind or of occluded gases if any, is of no account. The change of the diamagnetic susceptibility is to be attributed entirely to recrystallisation.

The method of melting and slow cooling has been used by several investigators to produce single crystals. McLennan and his collaborators[8] have cooled molten zinc over an interval of about 11 hours and obtained perfect single crystals. There is reason to believe that when the bismuth is cooled in small bulbs under the conditions obtaining in these experiments, crystallisation does not take place in any specific direction. The solid becomes an assemblage of several crystals. The susceptibility results obtained and recorded below justify these conclusions.

Focke[9] has given as the principal susceptibilities of bismuth the values 1·046 parallel to the main axis and 1·487 perpendicular to the main axis. His value for a heterogeneous aggregate of crystals is 1·340.[10]

3. *Results.*

The results are given in the following table :

Diam. of particle in μ.	χ before heat treatment.	After heat treatment.				Value of χ corrected for the oxide.
		χ_1	χ_2	χ_3	Mean χ.	
0·25	0·78	1·02	1·06	1·08	1·053	0·97
0·30	0·83	1·05	1·06	1·07	1·060	1·02
0·50	0·98	1·22	1·18	1·16	1·187	1·08
1·00	1·20	1·30	1·32	1·32	1·313	1·21
4·00	1·23	1·27	1·30	1·31	1·293	1·26
Regulus.	1·32	1·33	1·32	1·32	1·323	1·323

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[8] Proc. Roy. Soc., A, **121**, 9 (1928). See also Bridgman, ' Proc. Am. Acad., A, **60**, 305 (1925) and Kapitza, Proc. Roy. Soc., A, **119**, 358 (1928).

[9] Phys. Rev., **36**, 319 (1930).

[10] All specific diamagnetic susceptibility values in this paper are to be multiplied by 10^{-6}.

χ_1, χ_2 and χ_3 in the above table are the susceptibilities of the heated mass of bismuth in three mutually perpendicular directions. These values do not differ considerably from each other and from the mean value. This indicates that the bismuth mass may be taken to be an aggregate of several crystals.

It will be noticed that the regulus value does not show any change after heat treatment. But the colloidal powders show an increase. This is strikingly shown in the case of the finer particles. However in these cases the average susceptibility is still far below the mean value (1·323) for the regulus.

This is due to bismuth oxide still present in the bulb. The tartaric acid method in spite of great precautions does not seem to remove the oxide completely from the powder. While the bulbs containing the regulus bismuth were very clean after melting and cooling, the bulbs containing the powders became soiled inside because of the oxide separating out.

This fact, namely that there is still some oxide left behind even after tartaric acid treatment, shows that the curve shown on page 254 of paper I should really be less steep. Assuming that the susceptibility of the oxide is 0·14 nearly (see limiting value of the curve on page 246 of paper I) a calculation gives the values shown in the last column of the table for the susceptibility of the pure powders. The curve (*a*) in the accompanying figure shows the variation of χ with d (d being the diameter of the particles).

It will be seen that χ begins to decrease rapidly when d is nearly 1.5 μ. The curve (*b*) in the figure, drawn between χ and 1/d is still a straight line. This variation may be taken as a good estimate of the actual variation.

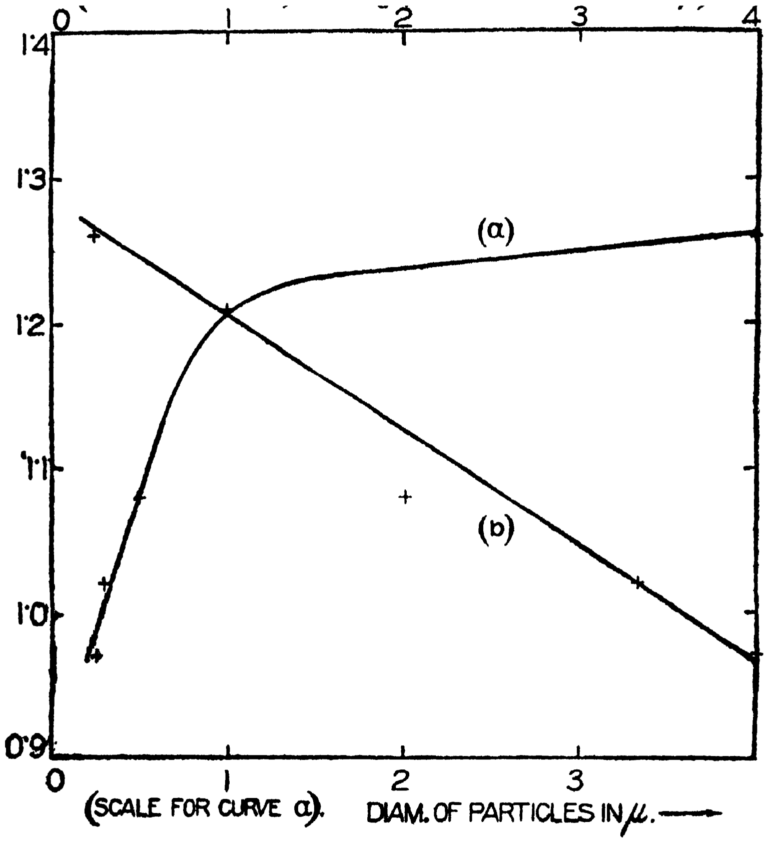

FIG. 1.

4. *Discussion.*

Our present knowledge concerning the variation of the magnetic susceptibility with particle size is limited only to bismuth and graphite. We have no other evidence except an observation by Vaidyanathan[11] on colloidal gold. In the absence of details regarding this investigation, one cannot draw any conclusions from this observation. Only bismuth and graphite and perhaps antimony seem to show distinctly anomalous diamagnetism.

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[11] Nature, 128, 802 (1931).

Mention was made in paper I that the fall of χ with particle size may be explained by increased internal stress on mechanical colloidization. This followed as a result of the experiments of Honda and Shimizu.[12]

The results of Bitter and Foladare [13] on similar lines indicate that magnetic susceptibility is structure sensitive. Lowance and Constant [14] extended their experiments and showed that the structure sensitiveness of the magnetic susceptibility was due to the partly bound electrons, the free and the completely bound electrons being structure insensitive. It is also known from the work of De Haas [15] that these partly bound electrons also account for part of the electric conductivity.

It is highly probable that the structure sensitive electrons are the same as Richardson's structure electrons since the secondary electron emission and the soft X-ray discontinuities which probably arise from these electrons are also dependent on the surface structure.[16]

Bismuth is interesting from other considerations. Goetz [17] recently studied microscopically the structure of fresh faces of bismuth single crystals and the growth of etching on such surfaces. He finds that the bismuth crystal consists of blocks of a definite size, these blocks being the smallest unit above the lattice unit in the crystal. The side of the elementary pyramid was found by him to be 1·4 μ. Goetz and Hergenrother [18] have investigated the question carefully and they show a distinct difference between the lattice expansion and the macroscopic expansion. The former was found to follow closely Gruneison's postulate (co-efficient of expansion varying directly as the specific heat) while the latter remained constant over a large range of temperature and began to decline rapidly at about 30 or 40 degrees below the melting point. The expansions were no doubt obtained parallel to the main axis of the crystal but the results are capable of extension in other directions.

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[12] Nature, **126**, 990 (1930).

[13] This work is referred to in ref. (14).

[14] Phy. Rev., **38**, 1547 (1931).

[15] Nature, **127**, 335 (1931).

[16] Proc. Roy. Soc., A. **128**, 63(1930).

[17] *Loc. cit.*

[18] *Loc. cit.*

The idea of a macroscopic structure superposed on the lattice structure is a very surprising result but it accounts for a number of observations.

It is a good coincidence that the diamagnetic susceptibility begins to decrease when the particle size reaches a value of 1·5 μ, *i. e.*, when the parameter is nearly equal to that of the macroscopic unit or elementary block of bismuth.

It appears also reasonable to attribute the macroscopic structure to the partly bound or structure electorns. These electrons may have very large orbits. The disposition of the orbits of the outer lattice electrons gives the cleavage face of the lattice structure. In the same manner the disposition of the structure electrons in bismuth may account for the cleavage faces of the mosaic structure and also for the high diamagnetism.

Further work is being done in connection with these problems.

6

X-Ray Analysis of the Structure of Diphenyl

By

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(Plate IV)

(*Received for publication, 7th March, 1932*)

ABSTRACT.

Intensities of X-ray diffraction from the diphenyl crystal do not correspond to the arrangement of molecules along any cell-face. It has been found however, by the " trial and error " method that the plane of the molecule is nearer to the *b-c* plane than the *a-c* plane. The correct position is obtained, by giving two successive rotations first about the *c*-axis and next about the *b*-axis to the extent of 32° and 20° respectively. In conformity with the space group C^5_{2h} the rotations of the two molecules are the same about the *b*-axis but equal and opposite about the *c*-axis. The two benzene rings in each molecule are flat regular hexagons lying in one plane. The distance between the consecutive carbon atoms in each ring from centre to centre is 1·42 Å whereas the length of the C-C bond connecting the two benzene rings is 1·48 Å. The results are quite in accord with the optical and magnetic measurements.

1. *Introduction.*

The study of diphenyl among the aromatic compounds is of interest as it provides an indirect evidence on the nature and symmetry of the benzene ring. Direct attack on crystalline benzene itself having been beset with experimental difficulties, diphenyl was the simplest of the hitherto-unattacked aromatic compounds to choose and a complete analysis of its structure was therefore desirable.

The nature and dimensions of the unit cell of the diphenyl crystal were long ago determined by Bragg.[1] Mark and Hengstenberg[2] have also determined the shape and size of the unit cell with dimensions $a=8{\cdot}22$ Å ; $b=5{\cdot}69$ Å ; $c=9{\cdot}5$ Å ; $\beta=94{\cdot}8^\circ$; Clark and Pickett[3] arrived at nearly the same values independently in course of their X-ray investigation on diphenyl derivatives. They have assigned the diphenyl crystal to the monoclinic prismatic class with the space-group C^5_{2h}. But there is one remark which we may make in this connection. In Groth's crystallography[4] the c-axis is given to be more than three times the value as obtained by Mark and Hengstenberg. As the latter have determined the c-axis from higher orders of reflexion from c-face assuming β and therefore indirectly, it was worth while to determine the c-axis from the rotation-photograph about c-axis. From consecutive layer-lines in the rotation-photographs about c-axis, the length of the c-axis is found to be 9·47 Å which agrees quite well with Mark's value. Mr. Biswas[5] of the Geological Department, Calcutta University, has made goniometric measurements with the diphenyl crystal. He has pointed out in a note that the face r is really $20\bar{1}$ instead of 101 as given by Mieleitner and recorded in Groth's. If r is taken to be $20\bar{1}$, $\frac{c}{b}$ comes out to be 1·67 quite in agreement with the ratio given by X-ray work.

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[1] Bragg's X-rays and Crystal Structure, p. 251, Chap 14 (1925).

[2] Zeit. Krist., 70, 283 (1929).

[3] Proc. Nat. Acad, Vol. 16, No. 1 (1930).

[4] Chem. Krist., Bd. V, p. 7.

[5] Jour. Sci. Dept. Cal. Univ., Vol. 10.

The diphenyl crystal is monoclinic and contains 2 molecules per unit cell and hence 24 carbon atoms. As the crystal has four elements of symmetry, it is merely necessary to determine the positions of 6 carbon atoms. Neglecting the effects of hydrogen atoms (which is justifiable because compared to carbon atoms, they scatter six times less) the number of independent parameters to be determined is 18. In most of such cases, the two-dimensional Fourier analysis of W. L. Bragg[6] and the method of Ott[7] are both unsuitable, for while the former requires absolute intensities of a large number of reflexions and the choice of proper signs of the terms in the Fourier series, the latter involves a large number of unknown parameters. The method here is consequently the method of trial and error, the co-ordinate process having been employed.

The method employed in the X-ray analysis of the crystal-structure is an indirect one. At first, we guess some arbitrary configuration of a molecule or molecules in the unit cell and if that conform to the observed data, we conclude that the configuration conjectured is correct. In the case of diphenyl which consists of two benzene nuclei joined end on by C-C bond in the para-direction, we have to make also some assumptions consistent with evidences from other sources.

Now Raman and Bhagavantam[8] have concluded from a consideration of the magnetic properties of organic crystals that the configuration of the carbon atoms in the aromatic rings is very similar with those of graphite. This was later on corroborated by Mrs. Lonsdale's[9] complete analysis of hexamethyl benzene and Dr. Banerji's[10] analysis of the structure of naphthalene and anthracene. It seems plausible therefore to assume that the benzene ring in aiomatic compounds is flat and is not puckered; but, if at all, to the extent of not more than 0·1 Å from the mean plane.

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[6] W. L. Bragg, Proc. Roy. Soc., Vol. 123, p. 537 (1929).

[7] Ott. Zeit. Krist. 66, 136 (1928).

[8] Ind. Jour. Phys., Vol. 4, Part I, p. 57 (1929).

[9] Lonsdale, Proc. Roy. Soc., 123, 494 (1929).

[10] Ind. Jour. Phys., Vol. 4, Part 7, p. 557 (1930

While the investigation was in progress, Smythe's report[11] on dipole moments appeared. From the absence of dipole moments in the para-dinitro, para-dichloro derivatives of diphenyl and on the assumption of the plane structure of the benzene ring he concluded that the benzene rings in diphenyl lie in one plane and hence along the prolongation of the C-C bond. Narasimham[12] made some refractive index measurements with this crystal. Therein he finds that the direction of the minimum optical polarisability is near to the *a*-axis of the crystal. Ramanathan's[13] theory tells us that if the incident electric vector is along the normal to the plane of the molecule the refractive index is a minimum. This indicates that the plane of the molecule is nearer the *b*-*c* plane.

These observations were useful as auxiliaries and with due attention to them, we were carrying on the structure-analysis. Meanwhile, Mr. Krishnan, Reader in Physics, Dacca University, determined the diamagnetic susceptibilities of the diphenyl crystal and fixed the orientations of the benzene rings in the diphenyl molecule. That minimised the labour to a great extent. In this paper an attempt is made to show that the X-ray data independently taken, fitted in quite well with the orientations of the molecules in diphenyl as found out by magnetic measurements.

2. *Experimental.*

When diphenyl is dissolved in distilled alcohol and then allowed to evaporate under the atmospheric pressure, it gives six-sided plates with faces 001, 110, $20\bar{1}$ and sometimes 100.

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[11] Indst. and Engi. Chem., Vol. 23, No. 11, p. 1224 (1931).

[12] Ind. Jour, Phys., Vol. VI, Part 3, p. 233 (1931).

[13] Proc. Roy. Soc., Vol. 110, p. 123 (1926).

These crystals were first examined under the polarising microscope and either of the positions of diminution of light marked on the crystal. Afterwards the position of the b-axis was fixed both by measurements and calculations. Once the b-axis is fixed, the a-axis will lie on the tabular face of the crystal and be simply perpendicular to it. The c-axis will evidently be almost perpendicular to the tabular surface. Then with any chosen axis of the crystal as the axis of rotation, oscillation photographs were taken. For this investigation, a Scherrer X-ray tube run by a transformer was used. The anticathode was made of copper and hence copper K-radiation was employed. No filter was necessary to cut off Cu_{k_β} as it is much feebler than Cu_{k_α} and reflexions due to the latter were therefore easily distinguishable. Three separate photographs with the three axes made coincident with the axis of rotation in turn were taken. As plane parallel plate perpendicular to the beam was used for photographing the reflexions, the layer-lines are hyperbolas. Reflexions close to the primary spot were measured and the axes were determined with the help of the relation :—

$$l=\frac{n\lambda}{y}\sqrt{r^2+D^2}$$

where l ⟶ length of the axis
n ⟶ order of the layer-line
λ ⟶ wave-length of the X-rays used
y ⟶ distance of the spot from the equatorial line
r ⟶ distance of the spot from the centre
D ⟶ distance of the crystal from the plate.

D was determined by taking reflexions from rock-salt. Thus we get

$$a=8{\cdot}28\text{A}^\circ;\ b=5{\cdot}82\text{A}^\circ;\ c=9{\cdot}47\text{A}^\circ.$$

β is calculated from higher orders of reflection from c-face and is found to be 95° 18′.

The volume of the unit cell $= abc \sin \beta$.

Thus if N denote the number of molecules in the unit cell,
M „ the molecular weight of the substance
m_H „ the mass of a hydrogen atom
ρ „ the density of the substancc

we have

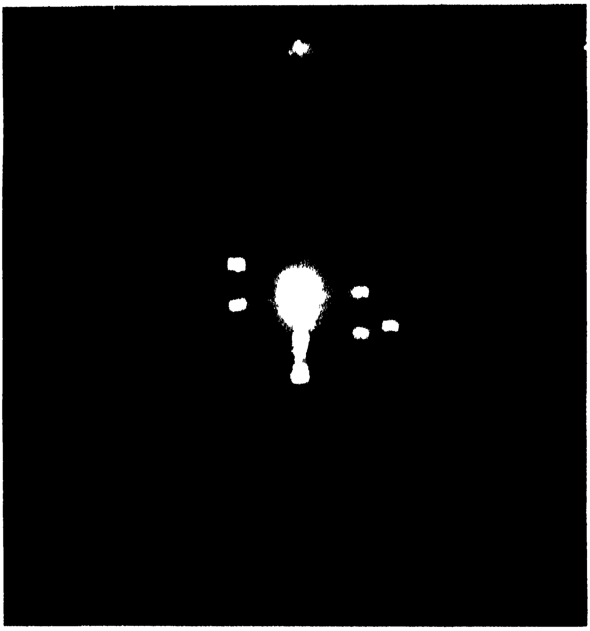
$$N = \frac{abc \ \sin \beta \times \rho}{M.m_H}$$

Taking $\rho = 1{\cdot}16$; we have $N = 2{\cdot}084$

i.e., the number of molecules per unit cell is 2.

The spots on the oscillation photographs were identified by measuring the spacings of the plane to which they are tentatively ascribed and comparing them with the calculated spacings. Confirmation is also obtained by calculation if such reflexions can occur at all under the experimental conditions. The integrated intensities of the equatorial layer-lines in the photographs were compared by means of a microphotometer as they were sharp lines. These are embodied in Table I. Since the intensity of reflexions from other faces depend on some unknown factors, they were recorded by eye-estimation. Hence they are qualitative.

It should be remarked here that considerable difficulty was experienced in reading the integrated intensity from the microphotometer curves. A blackness scale for the X-ray tube used was taken by plotting log t against log $\frac{d_0}{d}$ where t is the time of exposure, d_0 the intensity of the beam of light as it passes through the non-black portion of the plate and d the intensity of the same beam as it goes through the blackened portion. As in Röntgen rays intensity i is proportional to t, i can be easily obtained. The intensity i of any peak multiplied by the width of the same gives a measure of its relative integrated intensity.



(1) Rotation about C axis.

(2) Rotation about A-axis.

Rotation Photographs of diphenyl

Results :—

TABLE I.

Millerian indices.	Integrated intensity.	Molecular structure-factor observed.	Molecular structure-factor calculated.
001	72	·6	·61
002	100	1	1
003	5	·27	·24
004	20	·62	·62
005	14	·56	·52
012	4	·23	·21
015	5	·33	·24
023	5	·36	·34
203	10	·43	·44
401	6	·34	·39

TABLE II.

Millerian indices.	Remarks on intensity.	Molecular structure-factor observed.	Molecular structure-factor calculated.
013	Very weak	·10	·05
014	Very weak	·14	·09
022	Medium	·59	·58
$11\bar{1}$	Strong	1·17	1·09
111	Medium	·45	·36
024	Very weak	·15	·20
204	Medium	·73	·69
202	Weak	·30	·23
$20\bar{1}$	Very strong	1·79	1·86
201	Medium	·64	·59
$11\bar{2}$	Weak	·35	·33
112	Weak	·26	·18
$11\bar{3}$	Weak	·29	·30
$20\bar{5}$	Weak	·30	·35
400	Very weak	·14	·10
402	Very weak	·18	·13
403	Very weak	·26	·24

In Table II, since intensities were recorded by eye-estimation and comparison, remarks on the intensity of the reflexions were given in the second column. In every case the integrated intensity of the 002 reflexion is taken as 100 and that of the other reflexions are expressed in terms of it. In the third column, the structure-factor of 002 reflexion is taken as unity and for other reflexions it is given by the relation

$$\frac{F}{F_2} = \sqrt{\frac{\text{Sin } 2\theta \, (1+\cos^2 2\theta_2)}{\text{Sin } 2\theta_2 \, (1+\cos^2 2\theta)} \times \frac{\omega P}{\omega_2 P_2}}$$

where F ⟶ the molecular structure-factor for the plane in question.

θ ⟶ the glancing angle for that plane,

P ⟶ the integrated intensity,

and ω is the angular velocity of the crystal at the instant of reflexion.

ω is calculated by treating the oscillation as harmonic and using the relation

$$\omega = \omega_{max} \left[1 - \left(\frac{\theta}{\theta} \right)^2 \right]^{\frac{1}{2}}$$

where θ is the angle of reflexion and θ_0 the amplitude of oscillation. The terms with suffix 2 refer to reflexion 002.

3. *The Nature of the Benzene Rings in Diphenyl.*

From what has transpired in the structure-analysis of hexamethyl benzene, naphthalene and anthracene, it may be concluded that the benzene rings even in diphenyl are plane and for each of them the carbon atoms are arranged in a hexagonal ring with their diameters equal to 1·42 A° in conformity with the diameter of graphite. Since the diphenyl crystal belongs to the space-group C_{2h}^{5} and contains 2 molecules per unit cell, each molecule must have a centre of symmetry.

Two benzene nuclei joined by a C-C bond in the para-direction can have a centre of symmetry if they are in the same plane. So we will take the benzene nuclei in the diphenyl molecule to be plane and to lie along the prolongation of the C-C bond.

Starting with these assumptions as working hypotheses, we shall investigate into the orientations of the benzene rings round the crystal axes and then examine how far the deviations from them influence the reflexions from various planes.

4. *Theory and Method.*

The procedure was to compute the molecular structure-factors from the observed integrated intensities of the reflected spots and then to compare them with the calculated values. In order to calculate the structure-factors by treating the atoms as discreet points, we have made use of Robertson's [14] simplified interference formulae in case of crystals belonging to the space-group C_{2h}^5 and containing 2 molecules per unit cell. The expressions are

$$S=4\sum_{p=1}^{p=n} \operatorname{Cos} 2\pi \left(\frac{hx_p}{a}+\frac{lz_p}{c}\right) \operatorname{Cos} 2\pi \frac{ky_p}{b} \text{ when } h+k \text{ is even} \ldots \quad (1)$$

and

$$S=4\sum_{p=1}^{p=n} \operatorname{Sin} 2\pi \left(\frac{hx_p}{a}+\frac{lz_p}{c}\right) \operatorname{Sin} 2\pi \frac{ky_p}{b} \text{ when } h+k \text{ is odd} \ldots \quad (2)$$

the summation extending over one crystal unit which is half the chemical molecule. Here x_p y_p z_p are the co-ordinates of the pth atom in the unit cell and the other terms have the usual significance.

The molecular structure-factor is then calculated from the geometrical structure-factor from the relation $F_m = F_a . S \ldots (3)$ Here F_m is the molecular structure-factor, S the geometrical structure-factor and F_a the atomic structure-factor which is obtained from the curve for graphite given in Lonsdale's paper.[15]

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[14] Proc. Roy. Soc., Vol. 125, p. 546 (1929).

If we leave out of consideration any orientation whatsoever of the benzene nuclei in diphenyl, there are evidently two ways of placing the molecule *i.e.*, the molecule is either in the *b*-*c* plane or in the *a*-*c* plane. Let us now try if either of the ways of placing the molecule represent the real state of affairs. In Table III below, the structure-factors for different planes are calculated by equations (1), (2) and (3) according to these two ways of placing the molecule.

TABLE III.

Millerian indices.	Molecular structure-factor.		Remarks on intensity.
	Mol. in 100.	Mol. in 010.	
001	17·7	17·7	Strong
002	30·8	30·4	V. strong
020	19·8	72	Weak
021	3·7	8·8	V. weak
022	26·2	16·5	Medium
027	24	6·9	V. weak
015	0	0	Weak
016	0	0	V. weak
200	98·4	12·3	Medium
400	52·8	10·8	V. weak
202	20·8	19·2	Weak
201	12·1	·78	V. strong
$20\bar{2}$	21·4	12·5	V. weak
$40\bar{2}$	14·1	21·4	Weak
$21\bar{1}$	0	0	Strong
$11\bar{1}$	5	9·2	Strong
111	4·9	8·2	Medium
$11\bar{2}$	1·4	14	Weak
112	1·4	6·7	Weak
210	0	0	V. weak
410	0	0	Weak
012	0	0	Weak
013	0	0	V. weak
310	30·8	19·4	Medium
201	10·5	·34	Medium
014	0	0	V. weak

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[15] *L*

The second and third columns of the table contain the calculated structure-factors considering the molecules to be placed along the *b-c* plane and the *a-c* plane respectively. In the fourth column only the remarks on intensity are given. Even though no conclusive inference can be drawn from the results tabulated therein, the discrepancies for some of the planes, specially those for which the structure-factor altogether vanishes, *i.e.*, the planes $21\bar{1}$, 210, 012, 013, 014, 015, 016, 410 etc., are significant. This definitely shows that the molecules can be neither in the *b-c* plane nor in the *a-c* plane. Trial was then made to see if any amount of puckering without any orientations of the molecules can bring about any improvement, but without success. The only possible inference left is that the molecules are inclined to the axial planes and we are now to determine these inclinations.

To consider this point, let us suppose M_1 and M_2 to be the two molecules in the unit cell of the substance under investigation. Since it belongs to the space-group C_{2h}^5, one of the molecules M_1 (say) has its centre of symmetry at the corner of the cell and the other M_2 at the position $\frac{1}{2}a$, $\frac{1}{2}$ b, o (taking any corner as the origin of reference). To start with let us place the molecule M_1 with its centre of symmetry at the origin of co-ordinates, its plane coincident with the *b-c* plane of the unit cell and then bring it to the correct position by the following successive rotations :—

(1) through θ about the *c*-axis

(2) through ϕ about the *b*-axis

(3) through ψ about an axis normal to the *a-b* plane which we call as c * axis.

Since M_2 is derived from M_1 by a glide plane reflexion, it should have rotations of $-\theta$, ϕ and $-\psi$ respectively.

To simplify matters, we would at first confine our attention to the rectangular system of axes. Let *a*, *b*, *c*

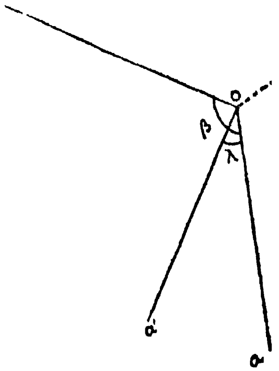


FIG. 1.

in the figure denote the axes in the monoclinic unit cell so that *b* is perpendicular to the plane of the paper in which *a* and *c* both lie. Draw *a′* in the plane of the paper at right angles to *c* so that the angle between *a* and *a′* is λ. Our method consists in finding out the final co-ordinates in terms of the rectangular axes *a′ b c* after operations (1) and (2) (omitting (3) for the present) and then changing them in terms of oblique axes.

Let $x\ y\ z$ be the initial co-ordinates of any atom in M_1. Then after rotating the molecule through θ about the *c*-axis in the direction *a* to *b* (which is taken as positive), they change into x_1, y_1, z_1,
so that

$$\begin{aligned} x_1 &= x\cos\theta - y\sin\theta \\ y_1 &= x\sin\theta + y\cos\theta \\ z_1 &= z \end{aligned}$$

If a second rotation of ϕ round the *b*-axis in the direction *c* to *a* (taken as positive) be given, $x_1\ y_1\ z_1$ change into $x_2 y_2 z_2$ where

$$\begin{aligned} x_2 &= x_1\cos\phi + z_1\sin\phi \\ y_2 &= y_1 \\ z_2 &= -x_1\sin\phi + z_1\cos\phi \end{aligned}$$

whence

$$x_2 = x \cos\theta \cos\phi - y \sin\theta \cos\phi + z \sin\phi$$
$$y_2 = x \sin\theta + y \cos\theta$$
$$z_2 = -x \cos\theta \sin\phi + y \sin\theta \sin\phi + z \cos\phi$$

Now if we like to express x_2 y_2 z_2 in terms of a b c, y_2 will evidently remain unaltered so that if we denote the final co-ordinates along a b c by X, Y, Z, then

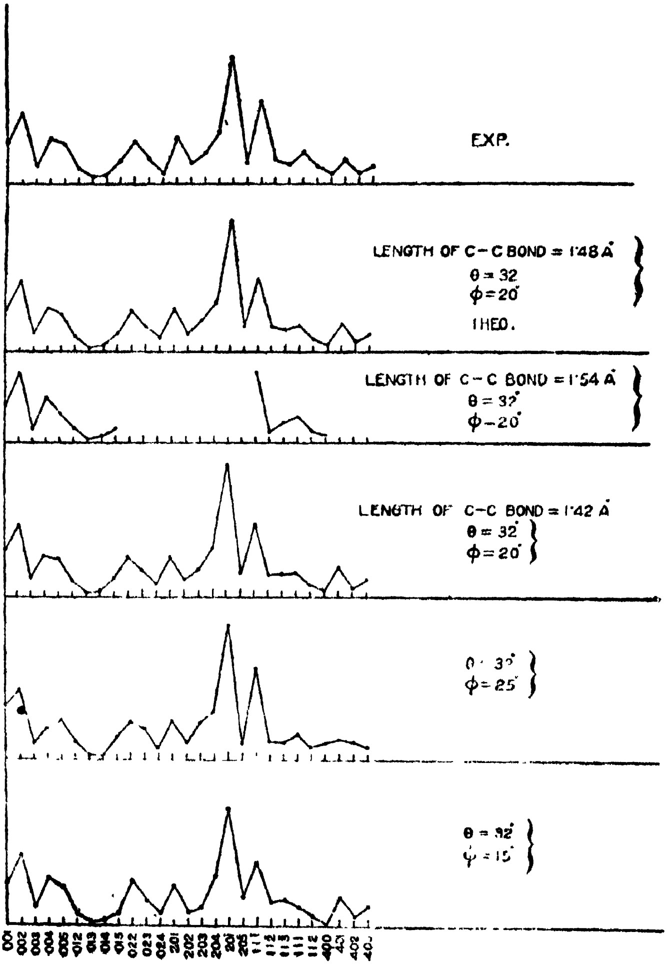
$$X = x_2 \sec\lambda; \quad Y = y_2$$
$$\text{and } Z = z_2 + x_2 \tan\lambda$$

In the same way, by rotating the molecule for the third time through ψ about an axis c^* an expression for calculating the final co-ordinates from the initial ones is obtained. But it is very complicated and so not included here.

In the beginning, we fixed our attention on the higher orders of reflexion from the c-face. By putting θ equal to zero and arbitrary values to ϕ (both positive and negative), we calculated the structure-factors from the final co-ordinates in that configuration and tried to secure an approximate fitting with the observed structure-factors. Then θ was changed so that all the reflexions in Table I gave structure-factors in accord with the observed ones. Best agreement was obtained for $\theta = 32^\circ$ and $\phi = 20^\circ$.

So far ψ is omitted. The higher orders of reflexions from the c-face are, however, independent of ψ. So in order to determine the parameter ψ, we will have to try other reflexions, specially those due to the planes of the general type $h\ k\ l$ and see how far the calculated structure-factors agree with the observed values. It is, however, found that the best agreement is obtained when ψ is put equal to zero. In the last column of Table II, the structure-factors were calculated by taking these values of θ, ϕ and ψ.

We have practically put our reliance on the measurements of the reflexions from 001 plane. It is, therefore, necessary to see how the variations in θ and ϕ affect the calculated values of the structure-factors. Besides, there are two other important points which require further investigation; one refers to the nature of the C-C bond joining the two benzene nuclei in diphenyl while the other enquires if there is any puckering, however slight, in the benzene nucleus itself. It is well-known to the chemist that this C-C bond is aliphatic and not aromatic and as such the length of the binding should be 1·54 Å. Thus with the orientations already fixed up, the structure-factors of the reflexions from various planes are calculated by varying this distance from 1·42 Å to 1·54 Å. The results are best shown graphically in the following. The first two curves give the experimental



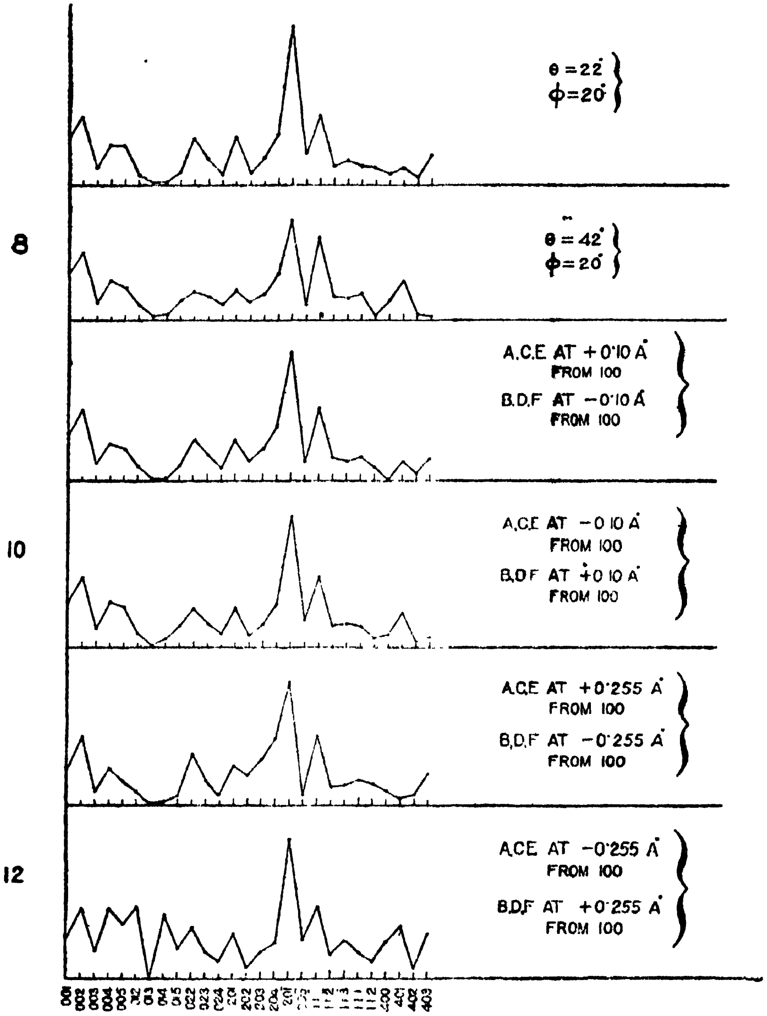


FIG. 2.

and theoretical values respectively of the structure-factors and the latter conform to the former as best as possible. In the second curve which represents the theoretical one, the length of the C-C bond is taken to be 1·48 Å. The third and fourth curves give the structure factors calculated with the same orientations but with the length of the C-C bond as 1·54 Å and 1·42 Å respectively. At certain positions of these curves, the deviations from the observed curve are quite apparent. The four other curves that follow are drawn by changing θ or ϕ with the values noted against them and taking the length of the C-C bond as 1·42 Å.

The last four curves, appended here, illustrate how the structure-factors vary if the structure is treated as puckered. The self-same orientations found out are also applied here to the molecule as a whole. In the first two curves of this group of four, the atoms are puckered to the extent of 0·1 Å from the mean plane which is taken as the *b-c* plane of the unit cell and in the last two they are puckered to the same amount as in diamond. There it can be easily seen that the coincidence between the observed structure factors and the calculated ones is altogether spoilt if the diamond type of the benzene ring is assumed. There are some points of disagreement with the observed curve even in the first two curves of this group which are revealed only on scrutiny. The best possible agreement evidently exists between the first and second curves.

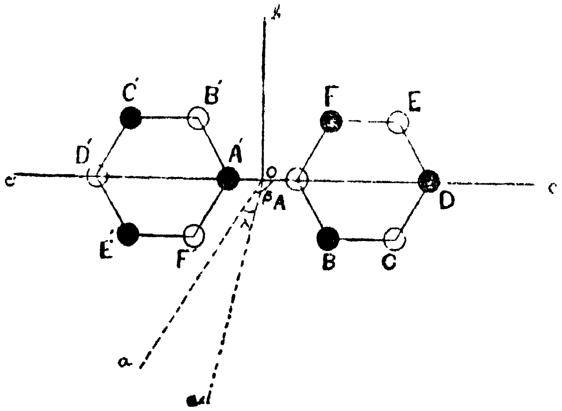


FIG. 3.

In order to calculate the final co-ordinates of the atoms in the puckered structure, what is done is to place the molecule first with its centre of symmetry at the origin of co-ordinates and its plane coincident with the b-c plane of the unit cell and then displace the atoms perpendicular to that plane one way or the other alternately to the extent desired. The initial co-ordinates of every atom in the molecule are thereby obtained. The molecule as a whole is then given rotations about *c* and *b* axes to the extent of 32° and 20° respectively and the final co-ordinates are calculated from the expressions already given. The structure-factors are then calculated as usual.

In Fig. 3, *a b c* denote the axes of the unit cell. The plane of the paper contains the *b-c* plane and hence also the mean plane of the molecule in its initial state, *a* lying in a plane perpendicular to it but inclined to *c* by β. a' is drawn in the plane containing *a*, *c* and at right angles to *c* so that the atoms are displaced initially along a'. The angle between *a* and a' is λ

$$\text{where } \lambda = \beta - \frac{\pi}{2}$$

5. *Conclusion.*

Very high order of accuracy cannot be expected here as excepting for a few reflexions, intensities were measured approximately for most of them so that with due regard to the uncertainties involved an error of the order of 10 per cent. is not unlikely in the determination of orientations. But there cannot be any denying the fact that the molecule in diphenyl is inclined to the cell-faces and no crystallographic axis is in the plane of the molecule. The orientations found out evidently indicate that the plane of the molecule is nearer the *b-c* plane than the *a-c* plane just as in naphthalene and anthracene and agree quite well with those given by magnetic measurements. The diamond type of benzene rings is shown to be wholly inadmissible. The amount of puckering, if there be any at all, is very slight and cannot in the present case be more than 0·1 Å from the mean plane 100. The distanec between the carbon atoms linking the two benzene nuclei in diphenyl is found to be 1·48 Å which is the mean of 1·42 Å and 1·54 Å. This seems to suggest that the C-C bond here is neither strictly aromatic nor strictly aliphatic but is certainly influenced by the presence of the two benzene rings.

My best thanks are due to Prof. Sir C. V. Raman, Kt., F.R.S., N.L., for his kindly suggesting the problem and taking keen interest in the work. I also acknowledge my indebtedness to Mr. Krishnan, Reader in Physics, Dacca University, for his many valuable suggestions.

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On the Raman Spectra of Piperidine, Ethyl Alcohol and Acetone

BY

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(Plate V)

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ABSTRACT.

The Raman spectra of piperidine, ethyl alcohol and acetone have been studied carefully with a view to record the faint lines and to compare these Raman spectra with the infra-red absorption curves for these substances. Solutions of *o*-cresolphthalein and uranine have been used as light filters in order to clean up the background in some regions of the spectrum and to assign the frequencies correctly. The wave-number shifts of the Raman lines observed are given below:—

Piperidine—140, 243, 400, 443, 755, 817, 857, 949, 1006, 1035, 1046, 1146, 1265, 1287, 1342, 1442, 2655, 2730, 2803, 2852, 2892, 2931, 3307 and 3339.

Ethyl Alcohol—437, 882, 1046, 1271, 1449, 1473, 2709, 2743, 2877, 2927 and 2972.

Acetone—392, 487, 527, 789, 903, 1065, 1221, 1358, 1423, 1705, 2689, 2857, 2923, 2964 and 3006.

Piperidine has given 14 new lines not recorded by previous workers, almost all of which are represented by maxima in the infra-red absorption

curve. Ethyl alcohol shows two new lines 2709 and 2743 and in the case of acetone, it is found that the line 2689 was assigned wrongly by previous-workers as 925 excited by 4358A.

1. *Introduction.*

Recently, Dr. Krishnamurti[1] has studied the Raman spectra of a few organic substances very thoroughly with his improved technique. As he has now taken up a different problem, the plates for piperidine, ethyl alcohol and acetone obtained by him were handed over to the present author for examination. The results are discussed in the present paper.

2. *Results.*

All the spectrograms were obtained with a Fuess glass spectrograph having a dispersion of about 16A per mm. in the region of 4358A. Iron arc spectrum was used for comparison. For each of the liquids, two spectrograms were obtained, one with a filter of uranine solution between the lamp and the liquid to weaken the region of the spectrum in the neighbourhood of 4358A, including the line itself, and another of *o*-cresolphthalein solution to weaken the 4046A region, as explained previously by Krishnamurti.[2] The *o*-cresolphthalein filter also cleaned up the background in the neighbourhood of 4916A and helped in recording the faint Raman lines in this region. The wave-number shifts of Raman lines for the liquids studied are give in Tables I, II and III. The complete tables showing assignment of the lines are given at the end of the paper.

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[1] P Krishnamurti, Ind. Jour. of Phys., *6*, 367 (1931).

[2] *Loc. cit.*

TABLE I.

Piperidine Frequencies.

No.	$\Delta\nu$	Intensity.	Values in μ.	Corr. infra-red max. in μ,
1	140	0	71·43	
2	243	0	40·9	
3	400	1	25·0	
4	443	2	22·6	
5	755	0(*b*)	13·3	13·7
	...	...	...	12·47
	817	5	12·25	12·20
7	857	0	11·67	11·63
	...	...	...	11·05
8	949	0	10·53	10·65
9	1006	1	9·94	10·18
10	1035	2	9·66	9·58
11	1046	2	9·54	...
	...	...	...	9·10
12	1146	2	8·71	8·62
13	1265	2	7·91	8·00
14	1287	2	7·59	7·61
15	1342	0	7·45	...
16	1442	3(*b*)	6.93	6·90
	...	...	...	6·35
	...	...	...	5·95
	...	...	...	5·30
17	2655	1(*b*)	3·77	...
18	2730	2	3·66	...
19	2803	2	3·57	...
20	2852	4	3·51	3·50
21	2892	2	3·46	...
22	2931	8(*b*)	3·41	...
23	3307	0(*b*)	3·02	3·0
24	3339	1(*b*)	2·995	

TABLE II.

Ethyl Alcohol Frequencies.

No.	Δν	Intensity.	Values in μ.	Corr. infra-red max. in μ.
1	437	½	22·9	
2	882	5	11·33	11·4
3	1046	2	9·56	9·7 to 9·2 broad
4	1096	2	9·12	
5	1271	2	7·87	7·8 to 7·0 broad
6	1449	3	6·90	
7	1473	½	6·79	
	...	...	...	6·20
8	2709	2	3·69	3·8 to 3·3 broad
9	2743	1	3·64	
10	2877	6	3·48	
11	2927	10	3·42	
12	2972	7	3·37	

TABLE III.

Acetone Frequencies.

No.	Δν	Intensity.	Values in μ.	Corr. infra-red max. in μ.
1	392	1½	25·5	
2	487	½	20·6	
3	527	2	18·98	
	...	...	...	13·1
4	789	5	12·68	12·65
	...	...	...	11·30
5	903	0	11·05	10·90
	...	...	...	10·40
	...	...	...	9·70
6	1065	1	9·39	9·10
7	1221	1	8·19	8·3
	...	..	...	7·6
8	1358	0	7·36	7·30
9	1423	3b	7·09	6·9
	...	...	...	6·6
10	1705	5	5·87	5·75
	...	...	...	4·72
11	2689	0	3·73	
12	2857	0b	3·50	
13	2923	10	3·42	3·42
14	2964	4	3·37	
15	3006	4	3·33	

3. *Discussion of Results.*

Piperidine was studied previously by Bonino and Brüll[3] who recorded only eleven lines. Table I shows that there

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[3] G. B. Bonino and L. Brüll. Gazz. Chim. Ital. 59, 675 (1929).

are twenty-four lines almost all of which are represented by maxima in the infra-red absorption curve. Considering the structure of the piperidine molecule, it is easy to see that there is hardly any mode of oscillation which is inactive, and Table I shows that this is actually the case, the only Raman line having no corresponding maximum in the absorption curve being a weak line at 1342. As the piperidine molecule is obtained by replacing a CH_2 group in the cyclohexane molecule by an NH group, the shape and mass of the piperidine molecule is almost the same as that of cyclohexane molecule. The difference between these two molecules is that there are two C-N bonds and one N-H bond in the piperidine molecule. It will be of interest to see whether the Raman spectra of cyclohexane and piperidine have any similarity with each other. The wave-number shifts of the Raman lines of cyclohexane recorded recently by Krishnamurti[4] are 381 ($\frac{1}{2}$); 425 (1), 695 (0), 804 (10), 1028 (8), 1156 (1), 1266 (5), 1344 ($\frac{1}{2}$), 1444 (5), 2351 (0), 2462 (0), 2630 (0), 2662 (1), 2695 ($\frac{1}{2}$), 2852 (8), 2889 (1), 2922 (8) and 2938 (8). On comparing these lines with those for piperidine given in Table I, it will be seen that there are many lines common to both. The lines 3307 and 3339 for piperidine are not present in the Raman spectrum of cyclohexane and are, therefore, due to N-H oscillation. It is interesting to note that these two frequencies are nearly the same as the two frequencies 3300 and 3380 of ammonia in the liquid state. The appearance of these two lines in the Raman spectrum of piperidine shows clearly the possibility of independent oscillation of two atoms of a small group in a large molecule with respect to each other, the frequency of such oscillation being determined solely by the nature of the two atoms and of the binding between them. It is, however, not easy to understand how one N-H group gives two Raman lines close to each other.

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[4] P. Krishnamurti, Ind. Jour. Phys., 6, 543 (1932).

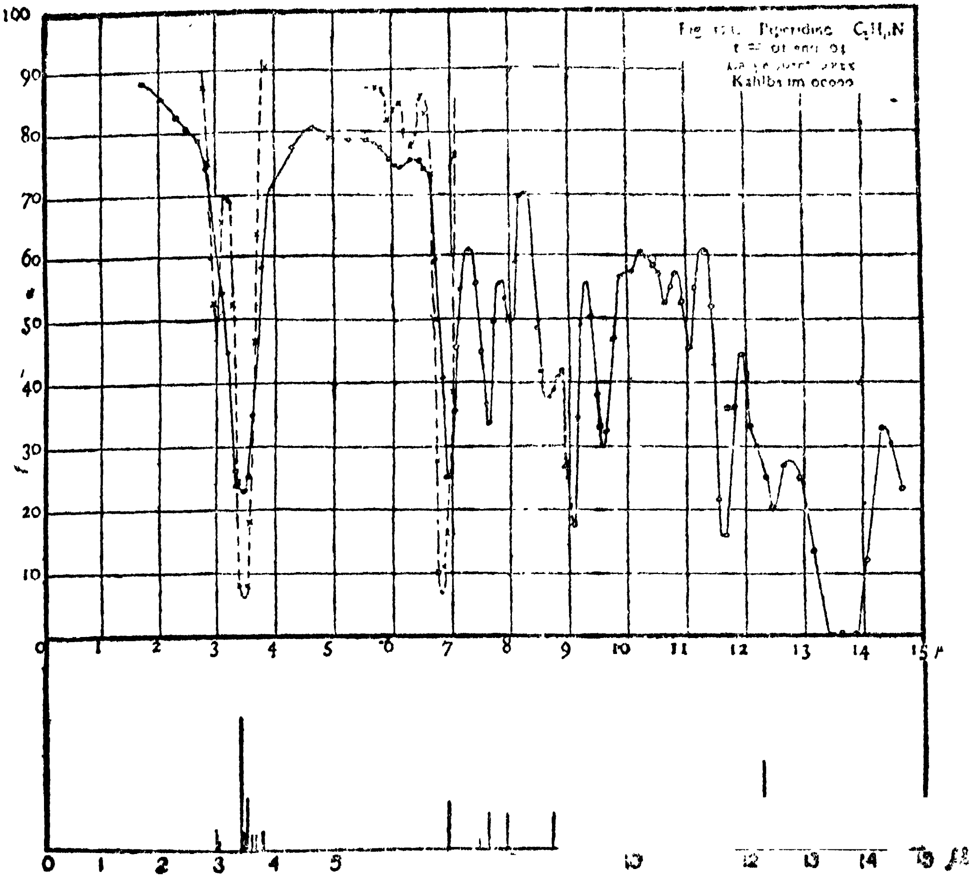

FIG. 1.

The infra-red absorption curve of piperidine given by Coblentz[5] is reproduced in Fig. 1 together with the Raman spectrum. The heights of the lines in the Raman spectrum indicate roughly the relative intensities of the lines. A glance at Fig. 1 shows that, except for the line 3·4 μ, there is hardly any resemblance between the relative intensities of the absorption peaks and those of the Raman lines. This is not difficult to understand from theoretical point of view, because an oscillation may produce a large induced electric moment without changing the polarisability of the molecule sufficiently to give an appreciable intensity of the corresponding Raman line but such an oscillation will give an intense peak in the absorption curve. It is only by comparing the complete Raman spectrum with the corresponding infra-red absorption curve that definite information about the nature of oscillation of the molecule giving any particular Raman line can be obtained.

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[5] Coblentz, Investigations of Infra-red Spectra, Carnegie Institution of Washington, 1905, p. 275.

Ethyl Alcohol.

Ethyl alcohol was studied formerly by Ganesan and Venkateswaran,[6] Venkateswaran and Bhagavantam,[7] Dadieu and Kohlrausch,[8] Daure [9] and others. The wave-number shifts of the Raman lines due to ethyl alcohol observed by the author are recorded in Table II. Except the two lines 2709 and 2743 which are not recorded by any of the previous workers, all the other lines recorded in Table II only confirm the results of previous workers. There is no doubt as to the existence of the lines 2709 and 2743, because they are found to be excited both by the 4358 A and 4046 A. The author, however, fails to detect on the plates examined by him any line of wave-number shift 1360 which has been reported by Venkateswaran and Bhagavantam.[10] It appears to be a case of wrong assignment by the said authors because they have recorded this line only for the exciting line 4358 A which is found by the author to be actually a line 2931 excited by the 4077 A. This line was very much weaker on the plate with *o*-cresolphthalein filter than on the plate obtained with uranine filter. Had a line 1360 excited by 4358A actually existed, it would have coincided with the line 2931 due to 4377 A but on closely examining the plate obtained with uranine filter, no trace of such

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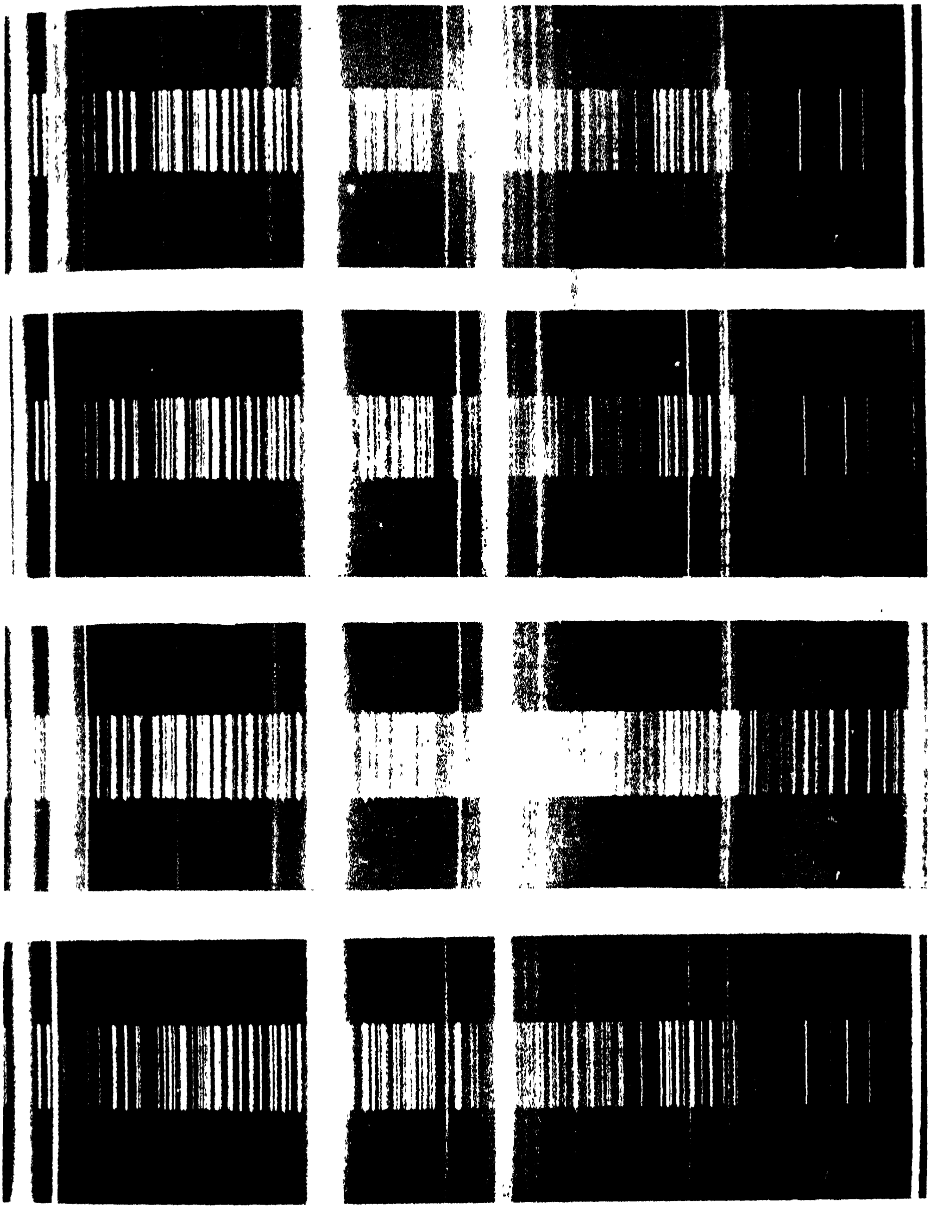
[6] A. S. Ganesan and S. Venkateswaran, Ind. Jour. Phys., 4. 195 (1929).

[7] S. Venkateswaran and S. Bhagavantam, Ind. Jour. Phys., 5, 129 (1930).

[8] A. Dadieu and K. W. F. Kohlrausch. Wien Bericht, 139, 79 (1930).

[9] P. Daure, Compt. Rend. 186, 1833 (1928).

[10] *Loc. cit.*



(a) Piperidine (Uranine filter) (c) Ethyl alcohol (Uranine filter)

(b) Ethyl alcohol (O–cresolphthalein filter) (d) Acetone (Uranine filter)

Raman Spectra.

a line excited by 4046 A was found though the plate was heavily exposed as is evident from the reproduction in Plate V. It appears therefore, that the line 1360 does not exist in the case of ethyl alcohol. The band 3416 is broad and faint, and appears to be exactly like the water band. It is a little difficult to say whether this band is due to the water present as impurity. A small percentage of impurity may give the strong lines due to the impurity.[11] The alcohol used in the present experiment was not purified carefully to get rid of water and it is, therefore, very probable that the band is due to water.

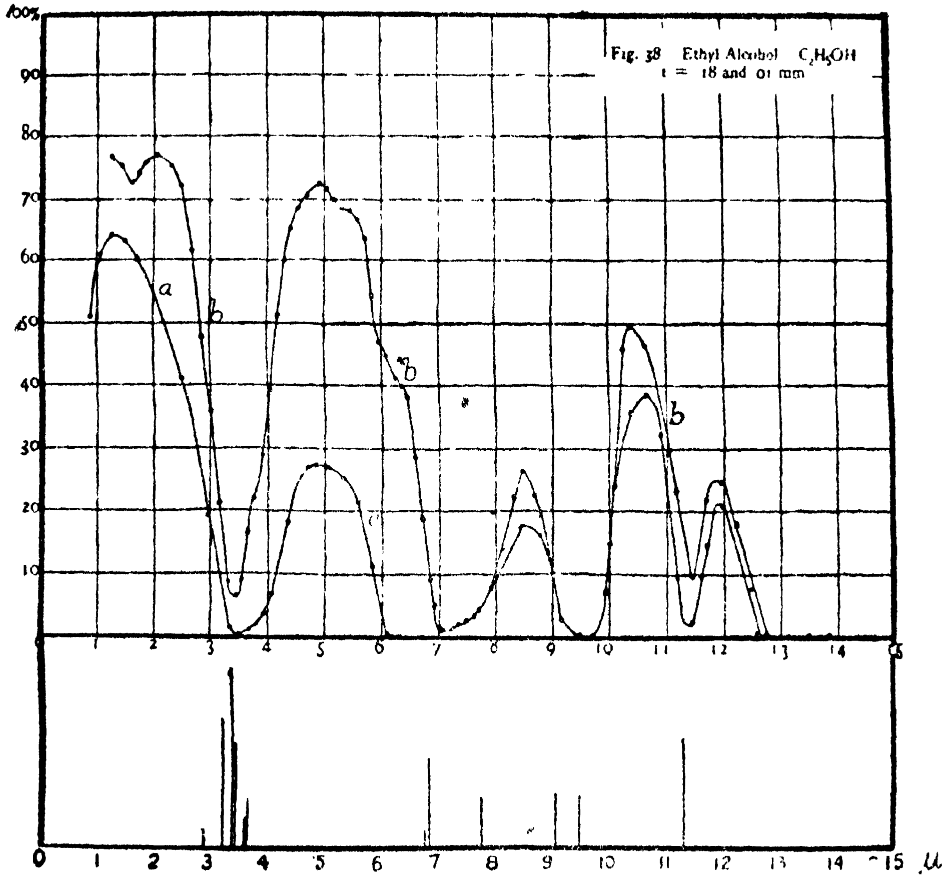


FIG. 2.

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[11] The author actually found all the strong carbon tetrachloride lines on a chloroform plate, the liquid used being accidentally slightly contaminated with carbon tetrachloride.

The infra-red absorption curve for ethyl alcohol given by Coblentz[12] is reproduced in Fig. 2 along with the Raman spectrum. The absorption peaks are not well resolved but still it can be seen that almost all the oscillations giving rise to the Raman lines are active and have corresponding maxima in the absorption curve.

Acetone.

Acetone was studied formerly by Dadieu and Kohlrausch,[13] Ganesan and Venkateswaran,[14] Dickinson and Dillon[15] and others. Of these, Ganesan and Venkateswaran and Dickinson and Dillon, have recorded a large number of lines not recorded by others. The wave-number shifts of the lines obtained by these authors as well as of those obtained by the present author are given in Table IV.

TABLE IV.

Acetone.

Ganesan and Venkateswaran.	Dillon and Dickinson.	Sirkar.
360 (0)	362 (2)	392 (1½)
544 (1)	492 (1)	487 (½)
795 (5)	530 (2)	527 (2)
940 (0)	788 (5)	789 (5)
1093 (0)	906 (0)	903 (0)
1231 (2)	928 (0)	1065 (1)
1365 (0)	1067 (2)	1221 (1)
1433 (2)	1223 (3)	1358 (0)
1718 (2)	1339 (0)	1423 (3b)
2857 (1)	1431(3br)	1705 (5)
2928 (8)	1711 (4)	2689 (0)
3037 (1)	1748 (1)	2857 (0b)
3121 (1)	2924 (5)	2923 (10)
3342 (0)	2967 (4)	2964 (4)
3663 (1)	3006 (4)	3006 (4)
3735 (1)		

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[12] Coblentz, Investigations of Infra-red Spectra, Carnegie Institution, Washington, 1905, p. 192.

[13] A. Dadieu and K.W.F. Kohlrausch, Wien. Bericht., **138**, 41 (1929).

[14] A. S. Ganesan and S. Venkateswaran, Ind. Jour. Phys., **4**, 195 (1929).

[15] R. T. Dillon and R. G. Dickinson, Proc. Nat. Acad. Sci., **15**, 699 (1929).

On comparing the results obtained by different authors as given in Table IV it is found that most of the lines are obtained by all the authors. The lines having wave-number shifts above 3037 recorded by Ganesan and Venkateswaran do not exist. The line 928 recorded by Dillon and Dickinson is found to be a line excited by 4046 A, having wave-number shift 2689. The light filters used in the present experiment helped very much in this particular case in the correct assignment of the line. Actually on the plate obtained with uranine filter, this line was stronger relative to the lines excited by 4358 A than on the *o*-cresolphthalein plate, showing that this line is excited by 4046 A. The line 1748 recorded by Dillon

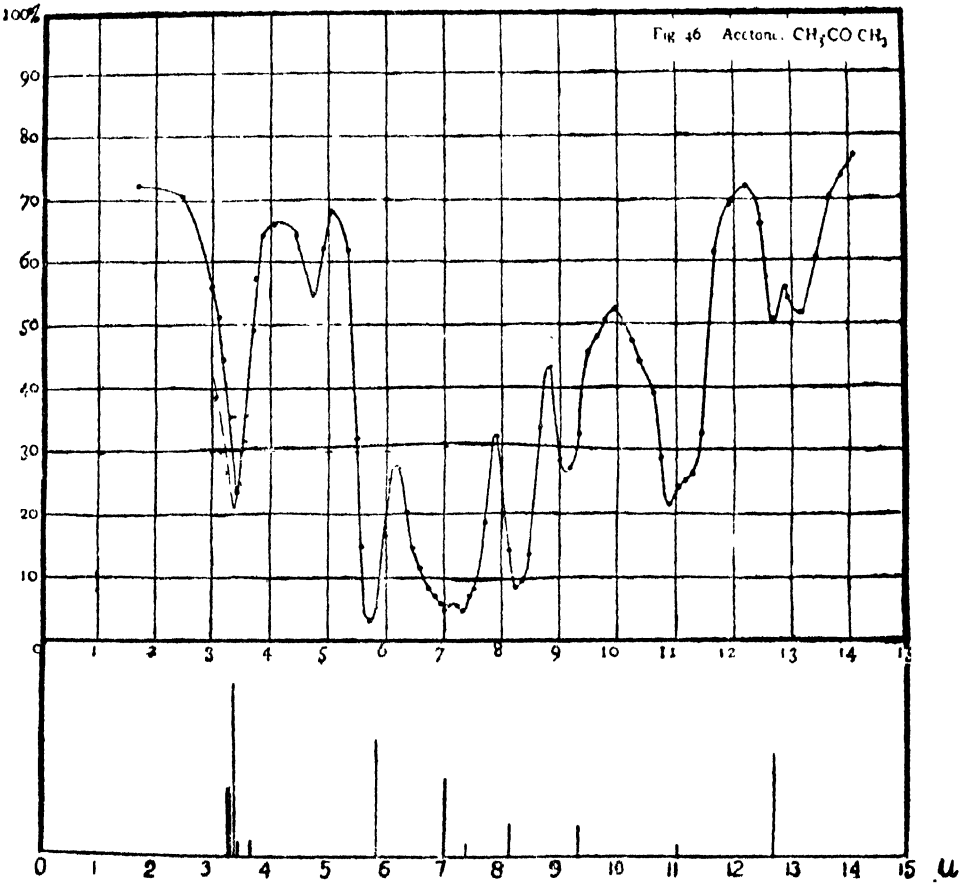

FIG. 3.

and Dickinson was not found on the plate examined by the author though the plate was fairly well exposed. The line therefore, does not at all or if it exists, the intensity is much smaller than that of line 906 and, therefore, cannot be recorded on a plate on which the line 906 is very faint. The line 2857 recorded by the author and also by Ganesan and Venkateswaran is not recorded by Dillon and Dickinson. There can be no doubt as to the existence of this line, because it has been found to be excited by both the lines 4046 A and 4358 A. The infra-red absorption curve for acetone given by Coblentz[16] is reproduced in Fig. 3 along with the Raman spectrum. It can be seen that in this case also, most of the oscillations giving rise to Raman lines are active and are represented by maxima in the absorption curve.

TABLE V.

Piperidine with O-Cresolphthalein Filter.

Wave-length of Raman line in I. A.	Wave number ν.	$\Delta\nu$	Intensity.	Assignment.
4385·0	22798·6	140	0	A
4405·0	22695	243	0	A
4435·6	22538·6	400	1	A
4444·1	22495·5	443	2	A
4506·6	22183·5	755	0*b*	A
4508·54	22174	821	0	a_1
4519·27	22121·3	817	5	A
4527·5	22081	857	0	A
4535·0	22044	2661	½*b*	B
4549·5	21971·3	2731	1	B
4558·2	21932·3	1006	0	A
4564·23	21903·5	1033 2805	2	A B
4566·45	21892·5	1046	2	A
4574·60	21853·7	2852	2	B
4583·1	21813·2	2892	1	B
4591·35	21774	2931	5*b*	B

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[16] Coblentz, Investigations of Infra-red Spectra, Carnegie Institution of Washington, 905, p. 200.

Piperidine with O-cresolphthalein Filter (continued.)

Wave-length of Raman line in I. A.	Wave number ν.	Δ ν	Intensity.	Assignment.
4612·5	21672·7	1265	2	A
4617·45	21651	1287	2	A
4623·0	21625	2891	0*b*	b_1
4629·5	21595	1348	0	A
4632·0	21582·9	2938	½*b*	b_1
4650·73	21496	1442	2	A
4672·0	21398	3307	0*b*	B
4679·0	21366·1	3339	1	B
4928·5	20284·5	2654	0*b*	A
4946·9	20209·0	2729	1	A
4965·0	20135·3	2808	1	A
4977·5	20084·8	2858	2	A
4986·5	20048·6	2890	1½	A
4996·51	20008·4	2930	3	A
5099·0	19606·2	3332	0	A

TABLE VI.

Piperidine with Uranine Filter.

Wave-length of Raman line in I. A.	Wave number ν.	Δ ν	Intensity.	Assignment.
4113·2	24305·3	400	0	B
4120·5	24262·1	443	0	B
4174·3	23955·1	756	0*b*	B
4184·9	23888·7	817	5	B
4191·44	23851·4	854	0	B
4208·3	23755·9	949 }	0	B
		+ 818 }		A
4218·6	23697·9	1007	1	B
4223·5	23670·4	1035	2	B
4225·42	23659·6	1046	2	B
4243·52	23558·7	1146	1	B
4265·37	23438·1	1267	2	B
4269·1	23417·6	1288	2	B
4270·0	23363·4	1342	0	B
4297·2	23264·4	1441	3*b*	B
4535·0	22044	2661	1 b	B
4549·5	21974·3	2731	2	B
4564·23	21903·5	2805 }	3	B
		1033 }		A
4574·60	21853·7	2852	4	B
4583·1	21813·2	2892	2	B
4591·35	21774	2931	3 b	B
4623·0	21625	2891	½ b	b_1
4632·0	21582·9	2933	1 b	b_1
4672.0	21398	3307	½ b	B
4679·0	21366·1	3339	2	B

TABLE VII.

Ethyl Alcohol with o-cresolphthalein Filter.

Wave-length of Raman line in I.A.	Wave number ν.	Δν.	Intensity.	Assign-ment.
4443·0	22501	437	½	A
4532·7	22055·7	882	5	A
4545·0	21996	2709	1	B
4552·0	21962	2743	1	B
4566·7	21892	1046	3	A
4580·0	21828	1096 }	4	A
		2877 }		B
4590·4	21778	2927	7	B
4600·0	21733	2972	5	B
4614·0	21667	1271	1½	A
4619·8	21640	2876	½	b_1
4631·5	21585	2931	½	b_1
4640·6	21543	2973	½	b_1
4652·2	21490	1449	3	A
4657·5	21465	1478	1	A
4696·0	21289	3416	0 b	B
4943·0	20225	2713	0	A
4951·0	20192	2746	0	A
4983·2	200	2876	3	A
4995·4	200	2925	5	A
5006·5	19968	2970	3	A

TABLE VIII.

Ethyl Alcohol with Uranine Filter.

Wave-length of Raman line in I.A.	Wave number ν.	$\Delta\nu$.	Intensity.	Assignment.
4120·0	24265	440	½	B
4196·8	23821	884	5	B
4225·0	23662	1043	2	B
4234·5	23608·9	1096	2	B
4266·3	23433	1271	3	B
4298·9	23255	1450	3	B
4302·9	23233·6	1472	0	B
4545·0	21996	2709	2	B
4552·0	21962	2743	2	B
4580·0	21828	2877	6	B
4590·4	21778	2927	10	B
4600·0	21733	2972	7	B
4619·8	21640	2876	1	b_1
4631·5	21585	2931	1	b_1
4640·6	21543	2978	1	b_1
4696·0	21289	3416	½b	B

TABLE IX.

Acetone with O-cresolphthalein Filter.

Wave-length of Raman line I.A.	Wave number ν.	$\Delta\nu$	Intensity.	Assignment.
4434·0	22546·7	392	1	A
4452·8	22451·5	487	0	A
4460·93	22410·6	527	2	A
4513·57	22149·2	789	5	A
4537·0	22034·8	903	0	A
4540·8	22016·4	2689	0*b*	B
4570·59	21872·9	1065	1	A
4575·6	21849	2858	0*b*	B
4589·54	21782·6	2923	6	B
4598·2	21741·0	2964	1½	B
4603·08	21718	1220	1	A
4607·13	21699·4	3006	2	B
4629·5	21594·6	2922	1½	b_1
4646·5	21515·6	1423	3*b*	A
4708·2	21233·6	1705	5	A
4978·34	20081·4	2857	0*b*	A
4993·8	20019·3	2919	5	A
5004·5	19976·5	2962	0	A
5014·5	19936·6	3002	0	A

TABLE X.

Acetone with Uranine Filter,

Wave-length of Raman Line in I. A.	Wave number ν.	Δ ν.	Intensity.	Assignment.
4135·2	24176	529	1	B
4180·23	23915·6	790	5	B
4213·65	23725·7	+ 788	1	A
4228·3	23643·5	1062	1	B
4257·0	23484	1221	1	B
4282·0	23347	1358	0	B
4294·2	23280·7	1425	3b	B
4540·8	22016·4	2689	½b	B
4575·6	21849	2858	½	B
4589·54	21782·6	2923	10	B
4598·2	21741·6	2964	3	B
4607·13	21699·4	3006	3	B
4629·5	21594·6	2922	2	b,

TABLE XI.

Symbol used.	Wave-length in I. A.	Wave number.	Intensity.
A	4358·34	22938·1	10,000
a_1	4347·50	22995·3	600
a_2	4339·24	23039·1	300
b_1	4077·84	24515·9	500
B	4046·56	24705·4	6000

In conclusion, the author wishes to express his indebtedness to Sir C. V. Raman, F.R.S., for his kind interest in the present work.

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CALCUTTA.

8

Polarisation of Raman Lines in Liquids

BY

S. BHAGAVANTAM

(Plate VI)

(*Received for publication, 12th March, 1932*)

ABSTRACT.

The paper describes the results of a study of the polarisation of a few typical Raman lines in some liquids. The method adopted is to expose the two components of each line for different times so that they are recorded on the plate with equal densities. Errors due to polarisation by oblique refraction at the prism surfaces, lack of transversality of the scattered beam and difference in the times of exposure of the two components are corrected for. The intense line 992 in benzene shows a depolarisation of 7%. The strong line in the series of tetrachlorides of carbon, silicon, titanium and tin arising from a symmetric expansion of these molecules exhibits a progressively increasing depolarisation; the actual values being 4%, 11%, 12% and 16% respectively. The depolarisation values of all the vibration lines studied in the present paper are found to lie within the range 0 to $\frac{6}{7}$. The rotational scattering appearing in the form of unresolved wings in carbon disulphide, benzene and thiophene is found to be depolarised to the extent of $\frac{6}{7}$.

1. *Introduction.*

On account of the extreme feebleness of the Raman lines and the consequent difficulty in applying the usual methods of photographic photometry, the various results hitherto published concerning the polarisation of these lines have been only of a qualitative nature. An attempt is made in the present paper to discuss the various possible sources of error and to arrive at certain definite polarisation values for a few typical lines in some simple liquids with the use of an improved technique.

2. *Experimental arrangements.*

All the liquids studied are contained in either big bulbs or wide tubes with flat ends and are illuminated by the light of a quartz mercury arc focussed into the liquid by means of a glass condenser. The two components of the scattered beam are focussed successively on to the slit of a spectrograph by means of a suitably oriented large nicol and a lens placed in the path of the scattered beam and photographed side by side on the same plate.

Sources of error:—Amongst the principal sources of error taken into consideration in the present investigation, the following may be noted.

(a) *Polarisation due to the instrument* :—A change is produced in the state of polarisation of the light entering the spectrograph owing to oblique refraction at the surface of the prism. This change is a constant characteristic of the instrument and may be determined by illuminating the slit with initially unpolarised light and observing the state of polarisation of the light that emerges out of the spectrograph.

(b) *Effect of slit width* :—Every partially polarised vibration line is accompanied by vibration rotation scattering on its either side which is depolarised to the extent of $\frac{6}{7}$. In order, therefore, to determine the state of polarisation of the true vibration scattering, the slit of the spectrograph has to be kept reasonably narrow so as not to include any appreciable part of the accompanying vibration—rotation scattering. If the slit is however very wide, then the results obtained refer to the aggregate scattering.

(c) *Correction due to lack of transversality* :—When the source of light and its image in the centre of the vessel containing the liquid are of a finite size, there is obviously present an error due to a lack of perfect transversality of the incident beam. This error depends in a complicated manner on the existence of various angles other than 90° which the scattered beam makes with all possible directions of the incident rays and cannot easily be evaluated. If on the other hand, light from a point source is focussed in the centre of the liquid and the scattered beam is taken from this focal plane, the error due to the above cause is entirely eliminated.[1] In order, therefore, to get an approximate idea of the correction needed a long tube of CCl_4 is illuminated successively with the full length of the mercury arc used in all the experiments and with the light from a mercury point source and the depolarisation of the $\lambda 4358$ line is determined after being scattered by the liquid using a wide slit. The following results are obtained.

Depolarisation of light scattered by CCl_4.

Incident light.	Sunlight.	Mercury point source.	5 inches mercury arc.
ρ	0·05	0·045	0·075

It will be noted that the value given in column 3 is higher than either the sunlight value or the point source value by about 0·03 or 3% . This correction becomes even less significant with increasing depolarisation of the line and may altogether be neglected for limiting values of depolarisation.

(d) *Correction due to difference in the times of exposure* :—The photographic blackening on the plate is not quite proportional to the time of exposure but a certain correction is needed. The general method adopted is to expose the two components of any one particular line for different times so that they are recorded on the plate with comparable densities. Under such circumstances ρ the depolarisation of the line is given by the relation

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[1] I. R. Rao, Ind. Jour. Phys., 2, 61(1927).

$$\rho = I_H/I_V = (T_V/T_H)^{0.86}.$$

It is easily seen that this correction is of the same order as that already found for lack of transversality in the case of low depolarisation values and is in the opposite direction. Under the actual conditions of the experiment, both these corrections are therefore neglected and the value of ρ is given as the ratio of the times for which the two components have to be exposed in order that they may be recorded on the plate with equal densities. The values so arrived at appear to be correct to about ±2% except in the case of highly depolarised lines.

3. *Results.*

A significant result obtained is that the intense rotational scattering exhibited by carbon disulphide, benzene and thiophene reaches the limiting depolarisation of $\frac{6}{7}$ in all cases. There is little doubt that this result is generally true and is in accordance with the theory of rotational scattering.

Benzene:—The following values are obtained for some of the lines in benzene.

ν:—	605	992	1584	1605
ρ:—	0·8	0·07	0·8	0·8

It may be noted that while the first and the last two lines are strongly depolarised, the one at 992 which presumably represents a symmetric oscillation of the benzene molecule shows a small but definite depolarisation of 7%. The striking difference between the states of polarisation of the 992 line and the double frequency at 1600 is of special significance.

The original interpretation suggested for the origin of this high frequency doublet was that it arises from a transverse motion of the hydrogen atoms. The contrary view that it represents the mutual oscillation of carbon atoms bound by double bonds while 992 is the corresponding frequency for single bonds has been put forward by Dadieu and Kohlrausch. The facts that the two are so differently polarised and that while 992 is a single sharp line, the higher frequency oscillation is actually double are not in favour of the latter view. It may also be mentioned here that in the series ethane, ethylene and acetylene the principal line representing the mutual oscillation of the carbon atoms remains perfectly sharp and shows no signs of either diffuseness or doubling as we go up the series although the frequecy increases in accordance with the increase in binding strength for double and triple bonds. It has also been found by the author[2] that the line of acetylene is very well polarised (depolarisation less than 20%) and there is little doubt that the corresponding lines in ethane and ethylene will be equally well polarised. In view of the above experimental facts it is clear that the existence of the very badly polarised doublet at 1600 in benzene cannot be taken as an evidence in favour of the presence of double bonds in its structure.

Carbon disulphide :—

ν :—	400	656	795
ρ :—	0·8	0·2	0·2

An interesting feature in this liquid is the existence of a weak line at 400 which has to be identified with a transverse oscillation of the carbon atom in the symmetry plane of the molecule. The oscillation is a degenerate one and is equivalent to an internal rotation of the carbon atom in that plane and its high depolarisation has evidently to be ascribed to these characters of the oscillation.[3]

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[2] Ind. Jour. Phys., 6, 319 (1931).

Formic acid :—In this substance, lines having frequency shifts 189, 673, 1050 and 1398 reach very nearly the limit of $\frac{6}{7}$. Others are all partially polarised amongst which the one at 1672 shows the best polarisation.

Thiophene :—In this substance, the prominent lines amongst those that reach the limiting value of 6/7 are 750 and 3080. All the other lines seem to exhibit relatively small depolarisation values.

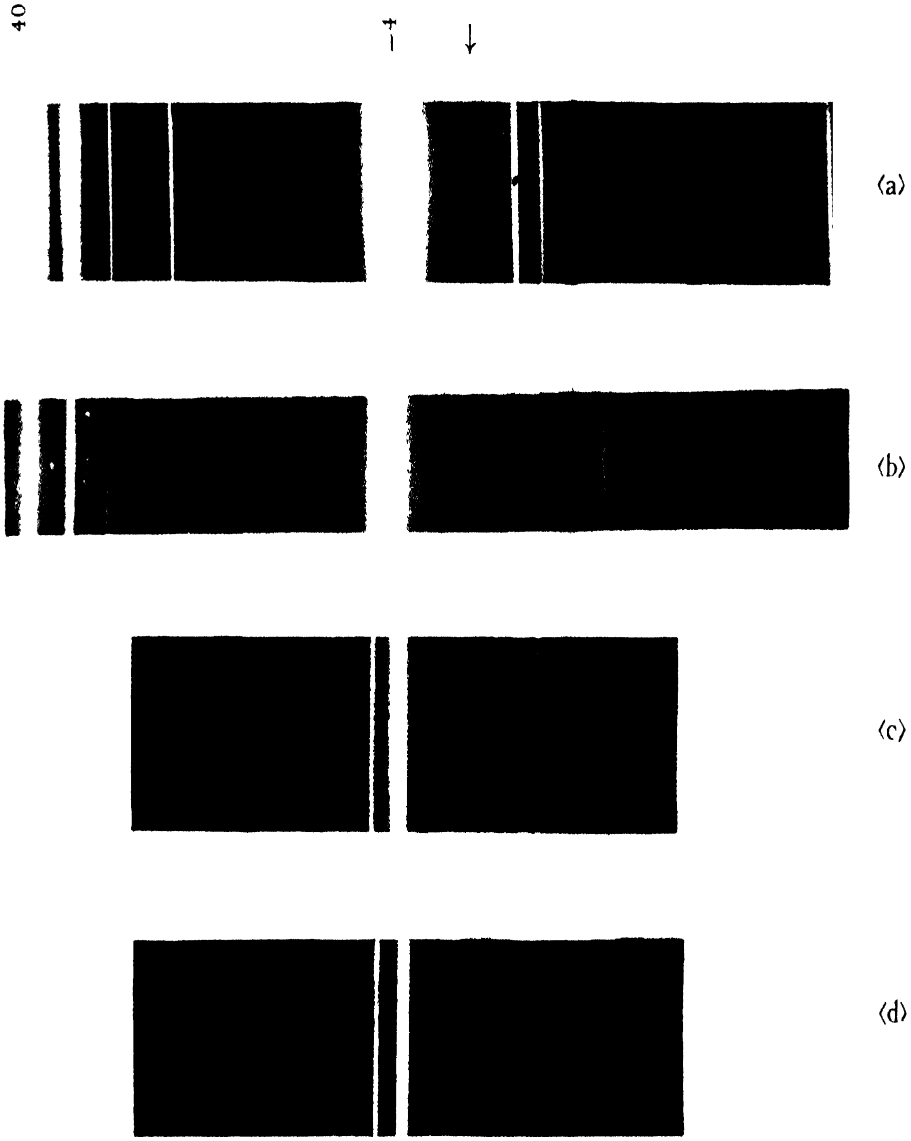
Tetrachlorides :—The following table contains the values for the various lines of the tetrachlorides of carbon, silicon, titanium and tin. They are somewhat different from those already published by the author[4] and are to be regarded as more accurate.

CCl_4		$SiCl_4$		$TiCl_4$		$SnCl_4$	
ν	ρ	ν	ρ	ν	ρ	ν	ρ
217	0·8	150	0·8	120	0·85	106	0·85
313	0·8	221	0·8	145	0·85	131	0·85
459	0·04	426	0·11	382	0·12	367	0·16
762 792	0·8	614	0·85	494	0·85	403	0·85

A notable feature is the interesting progression in the behaviour of the most intense line in this series. The depolarisation value increases from about 4% in carbon to 11% in silicon, 12% in titanium and 16% in tin. That these lines which correspond to a symmetric oscillation of the tetrahedral molecules exhibit a genuine depolarisation is not surprising

[3] S. Bhagavantam, Nature, 129, 167 (1932).

Ind. Jour. Phys., 5, 69 (1930).



(a) Carbon disulphide; (c) Carbon tetrachloride—Horizontal comp.

(b) Formic acid (d) Carbon tetrachloride—Vertical comp.

Raman Spectra.

in view of the fact that the Rayleigh scattering as well by these molecules shows a distinct depolarisation which is found to increase from about 5% in carbon tetrachloride to about 24% in tin tetrachloride. Such a genuine departure of the structure of these molecules from perfect optical symmetry is also evidenced from the existence of a rotational Raman scattering accompanying the Rayleigh lines. Figs. *c* and *d* in Plate VI are respectively the horizontal and vertical components of the light scattered by CCl_4 liquid, exposed for very different times. It may be noted that although the Rayleigh line in the horizontal component is actually weaker than the one in the vertical component, there appear strong wings on either side of it, while the vertical component is perfectly free from it. This clearly shows that the wing is of a genuine rotational origin and is, as may be expected, highly depolarised.

Contrary to the above results Cabannes[5] has recently reported that the intense line is equally well polarised in all the cases and is of opinion that the small depolarisation has to be attributed to the isotopes of chlorine and not to a genuine imperfection in the symmetry of the XCl_4 molecule itself. There is however nothing inherently improbable in the view that a tetrahedral molecule is not perfectly symmetrical especially if we recall the simplest case of methane. The appreciable imperfection of polarisation of the light scattered by this gas is now an established fact and the authour's recent work on the polarisation of the Raman lines in gases shows that the oscillation corresponding to a symmetric expansion of this molecule likewise shows a depolarisation of about 8%.

4. *Conclusion.*

Amongst the important conclusions that are reached from the present work, the following may be noted here.

Compt. Rend., **194**, 79 (1932).

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4. *Conclusion.*

Amongst the important conclusions that are reached from the present work, the following may be noted here.

Compt. Rend., **194**, 79 (1932).

The rotational Raman scattering appearing in the form of unresolved wings accompanying the Rayleigh lines in liquids is depolarised to the extent of 6/7.

In the vibration lines studied, there is no case for which the depolarisation exceeds 6/7, but there are however quite a number of them reaching this limiting value.

Vibration lines which presumably represent symmetric oscillations of various molecules exhibit small but definite depolarisation.

The molecules of carbon, silicon, titanium and tin tetrachlorides have a genuine *optical anisotropy*.

The doublet frequencies 1584 and 1605 in benzene showing practically the limiting depolarisation are ascribed to a transverse motion of the hydrogen atoms.

The author desires to express his best thanks to Prof. Sir C. V. Raman for his kind interest and guidance in the work.

9

A Note on the Variation of Faraday Effect With Concentration

By

P. K. Pillai.

In some recent experiments [1] on the magneto-optic rotations of the plane of polarisation of aqueous solutions of paramagnetic salts, the rotation due to the salt was derived from the simple additive relation that the rotation of the solution was the sum of the rotations due to the salt and the water contained. The present experiment was undertaken to see if the rotations derived by this simple relation were strictly proportional to the concentrations of the solutions. The salt chosen was cerium nitrate, and ten different concentrations were used, from one giving a strongly negative rotation to one giving a rotation very little less than that of pure water.

The usual electro-magnet arrangement was used with a triple field polariser and a Hilger analyser, the rotations being measured up to one minute of arc. A glass mercury vapour lamp with a neodymium glass filter was used as the source of light. A cylindrical glass cell 5 cms. long, with ground ends closed by micro cover glass, placed symmetrically between the pole pieces contained the liquid under investigation.

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[1] Ollivier, Comptes Rendus, **186**, 1001 (1928); **191**, 130 (1930).

The following table gives the results of the experiment.

TABLE I

Solution.	Density at 25°C. in gm./c.c.	Concentration in gm./c.c.	Rotation in degrees.	Water contained in one c.c. of solution	Rotation due to salt alone.
Water			2° − 54′		
A	1·449	0·741	−3−24	0·708	5°−27′
B	1·305	·497	−1−20	·808	3−41
C	1·230	·371	−0−13	·859	2−43
D	1·152	·237	+0−55	·915	1−44
E	1·123	·185	1−22	·938	1−22
F	1·083	·123	1−55	·960	0−53
G	1·067	·093	2−9	·974	0−40
H	1·048	·062	2−24	·986	0−28
I	1·035	·045	2−31	·990	0−21
J	1·027	·031	2−38	·996	0−14

The actual rotations given in the table were plotted against the concentrations and a straight line relation was obtained, there being a slight departure at low concentrations the points lying a little below the straight line. Verdet's constants, calculated by assuming that of water gave a similar relation with concentration. The rotations for the salt given in the last column of the table, calculated by the additive relation were plotted against the concentration and gave a straight line relation.

In this connection, it is interesting to mention that the values of Verdet's constants for ferric chloride given by

Becquerel [2] when plotted against the concentration do not give a straight line relation. Richards and Roberts [3] have found that aqueous sloutions of ferric chloride show anomalous rotatory dispersion near absorption bands. It is to be expected in a general way that substances which show anomalous rotatory dispersion would also show anomalies in the variation of Verdet's constants for wave-lengths not far removed from the absorption region, since absorption varies slightly with concentration. The following results taken from Roberts' [4] experiments on cobalt sulphate illustrate the point.

TABLE II

Solution.	Concentration in gm./c.c.	Verdet's Constant for $\lambda = 5893$ A.U.	Verdet's constant for $\lambda = 2482$ A.U.
Water		0·01309	0·1086
A	0·045	·01313	·1061
B	·069	·01306	·1056
C	·113	·01298	·1029
D	·232	·01309	·0965
E	·279	·01312	·0935

The Verdet's constants for $\lambda = 5893$, near the 5100 A.U. absorption band show considerable anomalies with respect to the concentration, being greater and less than the Verdet's constant for water, for different concentrations. On the other hand, the Verdet's constants for $\lambda = 2482$ A.U. far from the absorption region are nearly proportional to the concentrations.

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[2] Smithsonian Physical Tables, 1908, p. 289.

[3] Phil. Mag., 3, 770 (1927).

[4] Phil. Mag., 9, 361 (1930).

In conclusion, the author desires to express his grateful thanks to Prof. Sir C. V. Raman, F.R.S., for his kind interest and guidance.

10

Note on a New Rotating Commutator

BY

PROF. A. VENKAT RAO TELANG.

(Plate VII)

ABSTRACT.

A ring of thin ebonite sheet is mounted on a Phonic wheel. Fixed to the ring are two sets A and B of uniformly spaced radial sectors of metal sheet. The elements of A are between those of B and nearer the centre of the ring, so that the outer thirds of the elements of A and the inner thirds of those of B lie on a common circle. Three insulated metal brushes are mounted in a radial line to touch these sectors as the ring rotates, so that brushes 1-2 and 2-3 are alternately shorted through the elements of A and B respectively. The arrangement can be used to charge condensers or applied to other similar purposes. Using additional sets of brushes at different positions, on the ring, a number of similar commutating effects can be obtained with any desired variation in phase.

A rotating commutator is frequently employed for the accurate determination of small capacities. The accuracy of the results of such experiments depends on the possibility of maintaining a steady speed and accurate measurement thereof. There is a limit to the constancy of speed of a commutator driven by a small motor at high speed, and the chance of variation is the greater, the longer the speed has to be maintained. An alternative method has been the employment of an electrically driven tuning fork to move a commutating metal strip between two metal contacts. This is satisfactory only in so far as we could get a steady speed employing little power, and also different rates of commutation by the use of forks of suitable frequencies. But the efficiency of commutation depends on the efficiency and duration of the contact between the moving strip and the contacts on either side. Actual trial showed unsatisfactory results, the galvanometer deflection depending on the amplitude of motion of the fork.

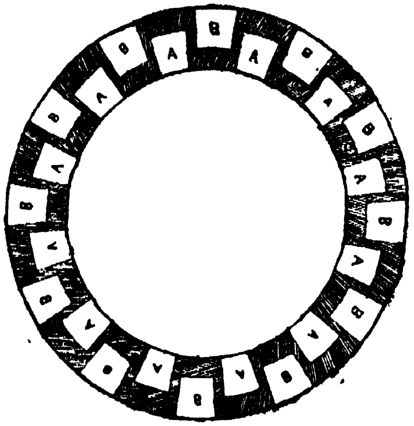


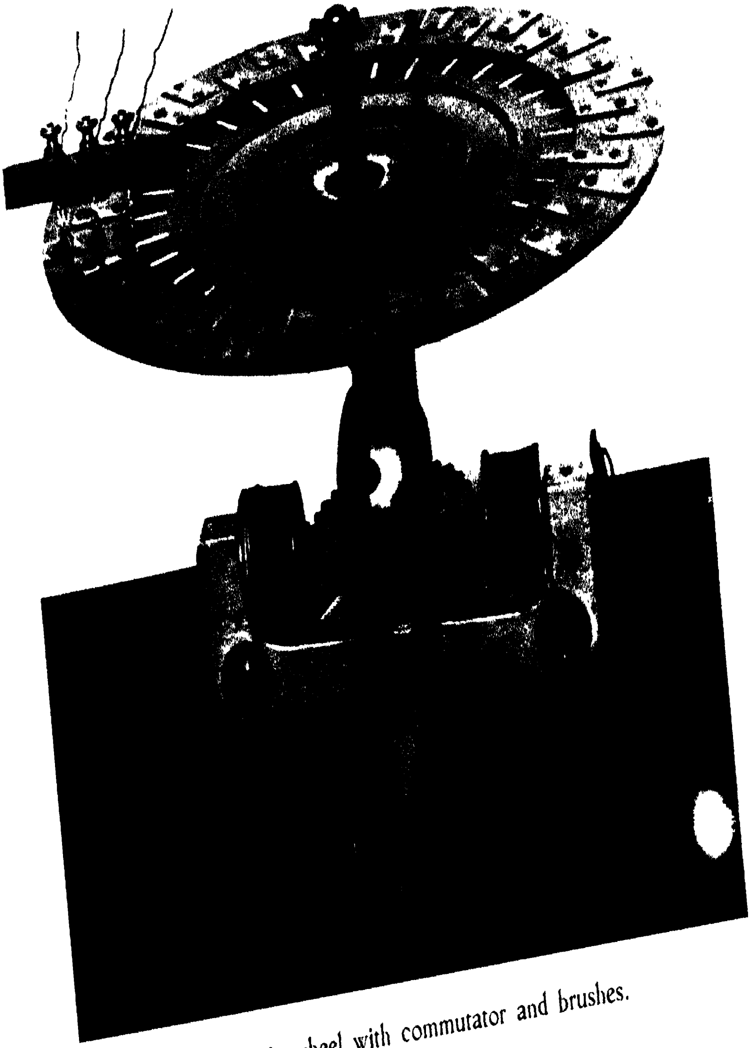
FIG. 1.

VULCANTIC RING WITH METAL SECTORS.

The present device secures a combination of the advantages of both, while eliminating the defects. A phonic wheel actuated by the intermittent current of an electrically maintained tuning fork is set rotating at a constant speed. This speed can be very accurately determined with the gear, counter and bell provided on the phonic wheel, and could be determined once for all for any fork.

A ring of thin vulcanite sheet 20-30 cms. in diameter and 4 or 5 cms. wide is fixed to the top of the phonic wheel so that its axis coincides with the axis of the rotating spindle (Plate IV). A number of sectors of thin brass sheet or thick tin foil about 3 cms. long and of suitable width are fixed radially on the ring, at equal intervals (Fig. 1). These sectors form two sets, the elements of one alternating with the elements of the second, and being nearer to the centre of the ring by about

PLATE VII



Phonic wheel with commutator and brushes.

1 cm. A set of three soft metal brushes[1] carried on an insulating rod are supported along a radial line to rub on these sectors as the ring rotates. The innermost brush touches only the sectors of the first set, the outer brush those of the second set only, while the middle brush touches all the sectors in succession. The sectors will thus alternately connect brushes 1-2 and 2-3....The brushes rubbing on metal give efficient contact and the duration of each contact is sufficiently long.

It is possible to use further sets of brushes simultaneously in other positions on the ring, and by their proper location, any desired phase difference can be introduced. By providing rings having different numbers of sectors, the frequency of the operation can be varied. Forks of different frequency can be employed. There is thus room for a wide range of frequencies, each of which could be exactly determined and maintained.

The special features of the apparatus may be listed as follows:—

(*i*) The speed is constant, and can be maintained so, indefinitely.
(*ii*) The speed can be very accurately determined.
(*iii*) A variety of frequencies can be obtained by the use of different forks and rings provided with different numbers of sectors.
(*iv*) The contacts are efficient and of sufficient duration.
(*v*) The power consumption for working the apparatus is quite low.

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[1] Tinsel has been found suitable for making these brushes,

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A Note on the Co-efficient of Viscosity of Liquid Sodium Amalgams

By

G. R. PARANJPE

Early in 1928, Mr. R. V. Barave was repeating a few of the viscosity measurements carried out previously by another worker in this Laboratory. He reported to me a very curious observation that the viscosity of an amalgam suffered a gradual lowering with time and that the original value of viscosity was regained by a mere mechanical agitation. Since no satisfactory explanation could be offered for this phenomenon on the basis of the existing theories, the matter was not pursued any further.

Since a considerable amount of research on this subject is being published wherein many physical properties including viscosity are studied, it is thought it would be worth while to give publicity to Mr. Barave's observations, for they have at least this important bearing on the viscosity measurements that the viscosity data (of previous workers) have now to be taken with considerable caution.

He prepared a liquid sodium-amalgam by the electrolytic method and attempted to measure its viscosity by making it flow through a capillary tube. Making arrangements for constant temperature, he measured the viscosity of the same amalgam every day for about three days and found that the viscosity gradually diminished. Perturbed over the inconstancy of what ought to be a constant, he shook his viscometer and mechanically stirred the liquid by passing it backwards and forwards a number of times and found to his surprise that the initial value was restored completely. Wondering as to what this could be, he prepared another amalgam of a different concentration and found that it also showed similar changes. His results are given below, the values being correct up to 1%.

TABLE I.

Time.	For amalgam A.	For amalgam B.
1st Day	0·01906	0·02757
2nd Day	0·01744	0·02151
3rd Day	0·01626	0·01669
	After shaking on the third	day
3rd Day	0·01908	0·02760

To pursue his observations still further, he prepared another amalgam, subjected it to the time change for two days, got its initial value restored by mechanical agitation and placed it again under observation to see if the time change still took place. As a result of observations for two days more, he found that the agitated amalgam also shows similar changes with time. The results of these experiments are given in Table II.

TABLE II.

Time.	For amalgam C.	For amalgam C (after shaking on the second day).	
1st Day	0·02027	0·02070	3rd Day.
2nd Day	0·01824	0·01567	4th Day.

Thinking that this might be due to the instability of the amalgams, *i. e.*, to the separation of Na from the amalgams, he prepared another amalgam by the same method and used one portion of it at once and kept the other in the storing vessel undisturbed for the time during which his experiments on the first portion were in progress. Now, if the change in viscosity was due to the separation of Na, such a separation must have already taken place in the second portion before its viscosity came to be measured and its initial value ought to be much lower than the initial value of the first portion. Actually he found that both the starting values were very nearly the same. Since his apparatus was perfectly air-tight, and the atmosphere in it was of an inert gas like pure dry nitrogen, he attributed this equality of both the starting values to the agitation the second portion suffered during its falling from the storing vessel into the viscometer. The results of these experiments are given below in Table III.

TABLE III.

Time (since preparation).	For the first portion.	Time (since preparation).	For the second portion.
1st Day	0·01846	4th Day	0·01887
2nd Day	0·01625	5th Day	0·01699
3rd Day	0·01560	6th Day	0·01539
	on shaking		
3rd Day	0·01850	6th Day	0·01890

It is clear from these experiments of his, that the viscosity of a liquid sodium-amalgam decreases continually with time and that mere mechanical agitation is sufficient to restore the starting value. And from this it follows that the viscosity measurements of at least liquid sodium-amalgams cannot be relied upon with any certainty unless the time factor is kept uniform throughout the series of measurements.

PHYSICAL LABORATORIES
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BOMBAY.

REVIEW

The Physical Properties of the Soil. By Dr. Bernard A. Keen. (The Rothamsted Monographs on Agricultural Science.) Pp. vii+380+2 plates. (London, New York and Toronto: Longmans, Green and Co., Ltd., 1931.) 21 *s*. net.

The concept that in the main, fertilisation is determined by chemical reactions governed by the nature and concentration of certain mineral substances in the soil, available within easy accessibility to the plant roots was the chief contention which Liebig elaborated in his famous memoir. Detailed work on manure absorption, and its subsequent behaviour showed; however, that soil reactivity is not wholly expressible in terms of simple chemical reactions. For example, as early as 1850, Way[1] found that when soil is treated with certain soluble salts of potassium, sodium, and ammonium, calcium is displaced and found in the wash solutions, and the corresponding constituents of the added salts are abstracted by the soil particles. Soon after, numerous cases were discovered, which showed that soil absorption was essentially a surface, a colloid phenomenon amenable in the majority of cases to Freundlich's adsorption isotherm. Results of subsequent research have brought out the very marked influence of the above physico-chemical factor on the utilisability of the available or potential plant food in the soil, and would appear therefore to be the chief determinant of its fertility. In the light of these developments, Dr. Keen's recent monograph on the 'Physical Properties of the Soil' giving a critical and a detailed account of the various mechanical, thermal, hygroscopic, electrical and

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[1] Russell, *Soil Conditions and Plant Growth*, 1927, London.

It is known that the last quantity is connected with the shape of the particles. This bears intimately on phenomena relating to the retention, and distribution of water, which together with water movements are of very great importance to plant life. Early workers ascribed these effects to surface tension and pressure effects within the soil interstices, soil itself being considered as a bundle of capillary tubes. A number of workers have also likened the water movements in the soil to the flow of heat or electricity. Corresponding to the electric current, and the potential difference, terms, *viz.*, the capillary conductivity, and the capillary potential (which denote, respectively, the facility with which water flows through soil pores, and the attraction between the soil and water) are introduced in the familiar Fourier's equations. These theories, however, have received but little support from experimental data. A completer analysis of the problem, due mainly to Haines, treats of the disposition of the water films about the points of contact amongst the soil particles. Considering typical configurations of the pore-space in a three-dimensional assembly of idealised particles, the different modes of water distribution resulting from a variation of the water content in the cellular space, impart to the system properties which have been found to be a good first approximation to the corresponding soil behaviour.

This varying moisture content plays an important part in determining the thermal characteristics of the soil such as the conductivity, the specific heat, the temperature, etc. The heat conductivity of the soil in the form of a continuous block is about seven times that of water. When present as powder it lies between one third and one half of that of water on account of the poor thermal contact. The heat is therefore carried chiefly by radiation and by air convection through the inter-granular space. With the introduction of *small* proportions of water, packing of the particles becomes closer by the surface tension of water, and thin conducting films are formed between neighbouring particles. This improves the conductivity beyond that of water, since that of the continuous soil material is called into play. As the amount of water is increased the soil particles move apart; the factor mentioned above becomes less important, and the conductivity of the system tends to that of water. It is also of very great interest to consider the specific heat of the soil for varying moisture contents. The specific heat of the soil when dry is usually in the neighbourhood of 0·2. This quantity would attain the water value only with a large proportion of water. It follows therefore that for small amounts of water in the soil, the increase of the specific heat with water is less rapid than that of its heat conductivity. "Within this range there is obtained best conduction of heat, and the greatest temperature rise for a given application of heat, and the soil is in its most effective state for supplying energy to the plants and the soil organisms,..............and which is also the point at which other considerations suggest that the soil is in the best condition for plant growth" (p. 311).

These are but a few samples from a very large amount of theoretical and experimental material packed by the author with great skill and insight within the limits of a moderate sized monograph. The volume is indispensable to students of agriculture as a science.

S. S. JOSHI

The Institute of Physics.

We are glad to be able to announce that an Indian Committee of the Institute of Physics has recently been formed in order to further the aims and objects of the Institute in this country. The names of the members of this Committee are :—

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2. Dr. P. N. Ghosh, Professor of Applied Physics, University College of Science, Calcutta.
3. Dr. H. P. Waran, Professor of Physics, Presidency College, Madras.
4. Mr. M. Owen, Principal, College of Science, Nagpur.

The Committee is still in its infancy and not much progress can be expected until it receives the support of other physicists in India. The following short note on the aims and objects of the Institute has been written with the object of eliciting such support from all those who are interested in the real development of physical science. If the response is gratifying, it is hoped to arrange for periodical meetings of Fellows and Associates at convenient times and places to correspond, for example, with the meetings of the Indian Science Congress. The aims of such meetings will be readily understood from the statement of objects and policy of the Institute.

The Institute of Physics was founded in 1918, with headquarters in London, with the object of securing the recognition of the professional status of the physicists, to urge the importance of physics in industry and to co-ordinate the work of all the Societies concerned with physical science and its applications. The work of the physicist has become increasingly important, both in science and industry, and, up to the time of foundation of the Institute, he was scarcely recognised as one of the professions. The engineer and the chemist were more wideawake, and their respective Institutes soon succeeded in raising the professional status of their members as well as safeguarding their interests. The need had long been felt for a corporate body analogous to the Institute of Chemistry which could represent the profession of Physics and strengthen the position of workers engaged therein.

The Institute grants Diplomas to Corporate Members indicative of high standard of professional competency in Physics. Corporate Members consist of two classes, Associates and Fellows. The authorised abbreviations indicating the class of the Institute to which any person belongs are "A. Inst. P." and "F. Inst. P." respectively. There is a small annual subscription for each class. Fellows receive the Journal of Scientific Instruments without further payment, while Associates pay small additional subscription of 10 *s*. 6 *d*. per annum for this Journal. In addition to the above Corporate Members, other persons possessing the requisite knowledge of, or interest in, Physics are eligible for Ordinary Membership.

A candidate who has attained the age of 21 years can be admitted to the Associateship either by or without examination. In the latter case, he must comply with one of the following conditions (*i*), (*ii*) or (*iii*) :

(*i*) If he has obtained a recognised degree or diploma and further pursued not less than one year's full time research in Physics.

(*ii*) If his research record is approved by the Board of the Institute as of such a quality as to justify the Board in exempting him from an examination.

(*iii*) If he has been or is responsible in a manner approved by the Board for valuable work in Applied Physics.

A candidate who is either an Associate or is possessed of the qualifications required for the Associateship is eligible for election to the Fellowship provided that, in addition :—

(*a*) He has carried out or been responsible for approved research work in Physics or its applications for not less than five years ; or

(*b*) He has been engaged in or responsible for manufacturing work involving a knowledge of Physics for not less than five years.

The Institute has been responsible for the publication of several lectures by well-known experts dealing with Physics in Industry. These refer to Physics in its relation to Engineering Science, Engineering Practice, Electrical Engineering, Ceramic Industries, Textile Industries, Metallurgy, Electrical Precipitation, Rubber Industry, Agriculture, Aeronautical Science, Navigation, Glass Industy, Food Industry, Photography, Utilisation of Fuel, Internal Combustion Engine, Astronomy and the Development of Wireless. These publications are obtainable at the offices of the Institute and no one who has read them can fail to observe the demands which the development of these various industries have already made upon the time and work of the physicist. No physicist can afford to be ignorant of the applications of his own subject to industrial progress. Below all this work for special industrial purposes there is, of course, a definite trend to gain further fundamental knowledge in various directions.

The present president of the Institute is Lord Rutherford. At the beginning of this year, there were 6 Honorary Fellows, 359 Fellows, 200 Associates, 85 Ordinary Members and 27 Registered Students on its rolls. Only 9 Fellows, 12 Associates, 5 Ordinary Members and one Registered Student are resident in India, while three further applications for Associate Membership are under consideration. It will be readily admitted that the total number of Indian members is far too low compared with the reputation and work of physicists in this country.

In the revival of Indian industries the physicist must take his part. The commercial community will continue to ignore us unless we are able to make our presence felt. The apathy of the physicist himself is proverbial, and it is only by joining together in one strong brotherhood that we shall be able to raise the level of our noble profession and insist upon the scientific advance of the nation. The opportunities offered to the Indian branch of the Institute call for the co-operation of all the leading physicists in the country. Further information regarding the Institute will be gladly supplied by any of the members of the Indian Committee. The prescribed application forms may be obtained from Mr. Owen at Nagpur.

Evidence for a Spinning Photon : I.

Intensity Relations in the Raman Spectrum of Hydrogen.

By

S. BHAGAVANTAM.

(Plates VIII, IX and X.)

(*Received for publication, 4th May, 1932.*)

ABSTRACT.

Measurements have been made of the intensity and polarisation of the lines in the Raman spectrum of hydrogen. The results when compared with those calculated from the quantum mechanics by Manneback show a beautiful agreement in respect of the relative intensity (both vertical and horizontal components) of the different lines in the P and R branches. But a striking disagreement with the conclusions of the quantum mechanics appears in respect of the intensities of the horizontal components of the P and R branches when compared with the horizontal component of the Q branch, the actual intensities of the former being much smaller in relation to the latter than the values given by theory. The results appear to indicate a definite failure of the accepted scheme of quantum mechanics. A suggestion is made as to the cause of the failure, namely, that in the quantum mechanics, the intrinsic spin of the photon has not been properly taken into account. A revised calculation on a modified basis gives results in agreement with experiment.

1. *Introduction.*

The belief that light consists of discrete and enumerable units or quanta rests upon certain phenomena, namely, the photo-electric effect, Compton effect and Raman effect which may be observed under suitable conditions when radiation falls upon matter. In each of these phenomena, the experimentally observed results may be described by regarding the case as one of encounter between a material particle and a quantum of radiation, and ascribing to the latter, certain dynamical properties. For instance, in the explanation of the photo-electric effect, the quantum is assumed to possess energy $h\nu$ which is absorbed and utilized in ejecting the electron from the atom. The additional assumption that the quantum possesses linear momentum $h\nu/c$ similarly serves to give an account of the Compton effect. Still another attribute for the photon, namely, the possession of an intrinsic spin or angular momentum $\pm h/2\pi$ appears to be necessary in order to make it intelligible why in the Raman effect a dumb-bell molecule such as H_2, N_2, O_2 may change its state of rotation as a result of an encounter with the quantum. Whether this spin of the photon and the exchange of angular momentum between it and the molecule are adequately taken care of in the existing theories of light-scattering will best become evident when we compare the facts observed in experiment with the results of the theoretical treatments. The exact experimental study of the Raman effect with the simplest molecules is thus of great importance, not only as a means of deciding the question whether the photon has an intrinsic spin or not, but also as a method of testing the correctness of existing quantum-mechanical theories of radiation.

The beautiful researches of Rasetti, Wood and others on the Raman spectra of the diatomic gases are well-known. These investigators, however, concerned themselves mainly with the frequency shifts observed in the spectra and their interpretation, and left untouched the very important question of the absolute intensity of the Raman radiations and their state of polarisation. A knowledge of these quantities and of their relationship to the intensity and polarisation of the Rayleigh scattering by these gases is fundamental to the subject. To fill this gap in our knowledge, the study of light scattering in gases with special reference to questions of intensity and polarisation was taken up by the present writer towards the end of 1930, and has been systematically continued ever since. From time to time, preliminary reports of the results obtained have been published in the Indian Journal of

Physics and in short communications to 'Nature.' The purpose of the present memoir is to describe in detail the technique which has been developed in the course of these investigations and to present *for the first time*, the results of a complete study of the Raman spectrum of hydrogen. The principal interest of these experiments is that it is now possible to make a comparison between them and the theory of light scattering developed by Prof. Manneback [1] for diatomic gases on the basis of the quantum mechanics. The results disclose a very good agreement in some respects with the theory but are in a remarkable disagreement with it in other respects. It is perfectly clear that the disagreement is fundamental and not due to any errors of experiment on the one hand or to any analytical defects in Professor Manneback's investigation on the other hand.

2. *Experimental Technique.*

One of the chief difficulties in the study of the Raman effect with gases is that of securing sufficient intensity of scattering for good photographs to be obtained with not excessively long exposures. Rasetti [2] obtained the Raman spectrum of hydrogen working with the gas contained in strong silica tubes at a pressure of 12 atmospheres and lighted by the λ2536 mercury radiation from a special type of water cooled arc. McLennan, Smith and Wilhelm [3] worked with liquid hydrogen preserved in transparent Dewar vessels and used λ4358 and λ4046 as the exciting radiations. In both the above methods, the mercury arcs are kept as close to the substance as possible in order to obtain a sufficiently intense scattering. The procedure is obviously unsuitable for investigating the various problems connected with intensity and polarisation, as for this purpose one has necessarily to use an incident parallel beam and make the observations at an angle of 90° with its direction dynamical properties. For instance, in the explanation of the photo-electric effect, the quantum is assumed to possess energy $h\nu$ which is absorbed and utilized in ejecting the electron from the atom. The additional assumption that the quantum possesses linear momentum $h\nu/c$ similarly serves to give an account of the Compton effect. Still another attribute for the photon, namely, the possession of an intrinsic spin or angular momentum $\pm h/2\pi$ appears to be necessary in order to make it intelligible why in the Raman effect a dumb-bell molecule such as H_2, N_2, O_2 may change its state of rotation as a result of an encounter with the quantum. Whether this spin of the photon and the exchange of angular momentum between it and the molecule are adequately taken care of in the existing theories of light-scattering will best become evident when we compare the facts observed in experiment with the results of the theoretical treatments. The exact experimental study of the Raman effect with the simplest molecules is thus of great importance, not only as a means of deciding the question whether the photon has an intrinsic spin or not, but also as a method of testing the correctness of existing quantum-mechanical theories of radiation.

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[1] C. Manneback, Zeit. f. Phys., *62*, 224 (1930) and *65*, 574 (1930).

[2] Phys. Rev., *34*, 367 (1929).

[3] Trans. Roy. Soc. Canada, *23*, 247 (1929).

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[1] C. Manneback, Zeit. f. Phys., *62*, 224 (1930) and *65*, 574 (1930).

[2] Phys. Rev., *34*, 367 (1929).

[3] Trans. Roy. Soc. Canada, *23*, 247 (1929).

Another important question of technique is that of eliminating parasitic light. The necessity for this is strikingly illustrated by the photographs obtained by McLennan, Wilhelm and Smith, in which relatively few lines, in fact only three or four of the strongest, are recorded, in spite of the fact that liquid hydrogen was employed and very well exposed pictures should therefore have been obtained. That the fainter lines do not appear on their plates is evidently due to their suppression by the continuous spectrum of the mercury arc reflected from the walls of the Dewar vessels containing the liquid hydrogen. It is, therefore, obvious that serious errors in the photometry of faint Raman lines would enter if parasitic light is not carefully avoided. Uneliminated parasitic light would in addition lead to grave errors in the measurement of the relative intensities of the Raman and the Rayleigh lines, by making the Rayleigh scattering appear more intense than it really is. An apparatus has been constructed with all the above points in view which enables very clear and well-exposed pictures of the Raman spectra of gases to be obtained with moderate exposures using glass spectographs.

A brief description of the apparatus already given in an earlier communication [5] will be included here for convenience (see Fig. 1).

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[4] K. S. Krishnan and A. Sarkar, Ind. Jour. Phys., 6, 194 (1931).

[5] Ind. Jour. Phys., 6, 319 (1931).

The gas is contained in a transparent silica tube having an inner diameter of $\frac{3}{4}''$ and an outer diameter of $1\frac{1}{4}''$. This is enclosed in an outer steel tube T for protection. A circular glass window contained between thick rubber washers is pressed against the plane end of the quartz tube by a steel screw cap. The steel tube has a slit $6'' \times \frac{1}{2}''$ cut out of it for illuminating the gas. The gas is admitted through a pin valve V attached to the screw cap C_2 at the back end of the quartz tube. An inclined black glass B is provided for securing a dark background. The outer surface of the silica tube is painted black leaving only a slit in the same position and of the same size as the slit in the outer steel tube for illumination of the gas. A system of painted apertures A is provided within the silica tube with the result that no light reflected by the walls of the tube enters the spectrograph. Pressures up to 50 atmospheres could be used in this apparatus and very good photographs obtained in about 40 to 50 hours' time using λ 3650, λ 4046 and λ 4358 as the exciting radiations.

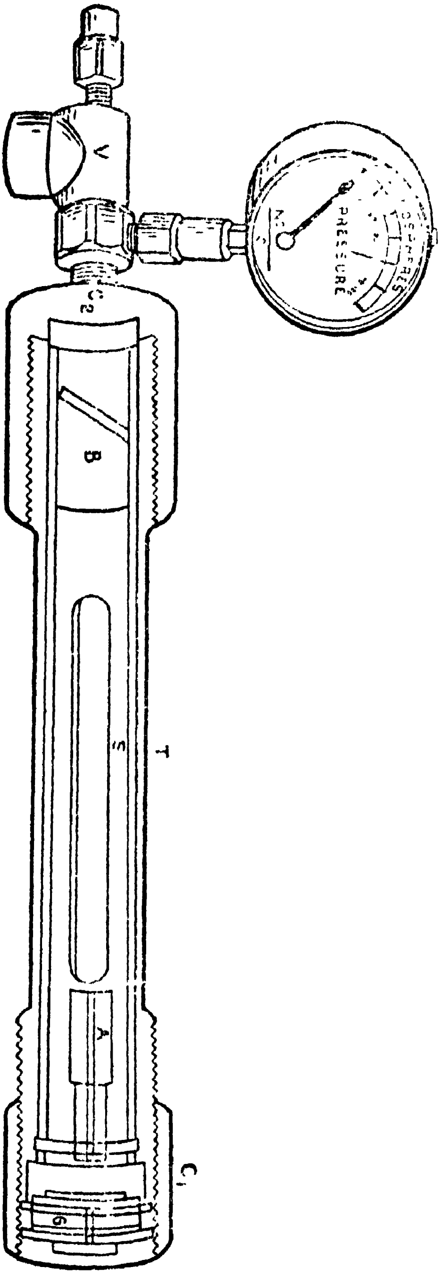

Fig.

The apparatus is used in conjunction with a 6-inch quartz mercury arc of the usual type. Light from this lamp is condensed by a large glass condenser into the gas tube. With such an arrangement, the parasitic light is much less than in the alternative plan of keeping the lamp directly above and in contact with the gas tube.

It may be mentioned here that for a comparison of the intensities of the horizontal components of the Raman and Rayleigh radiations or for a measurement of the state of polarisation of the Rayleigh scattering by itself, an even more rigorous elimination of the parasitic light is necessary and this can only be achieved with a different form of the apparatus to be described later.

3. *The Raman Spectrum of Hydrogen.*

Figs. (*a*) and (*b*) in Plate IX are obtained with the apparatus shown in Fig. 1 using pressures of 30 and 50 atmospheres respectively and an analysis of these photographs reveals the following frequency shifts for the H_2 molecule. A complete list of the observed lines and their assignments to the various exciting lines is given at the end of the paper as Table XII.

TABLE I.

Raman frequencies in hydrogen.

Transition.		Bhagavantam.	Rasetti.
n	K		
0 → 0	3 → 1	−587·0	−587·3
	2 → 0	−354·0	−354·5
	0 → 2	354·5	354·1
	1 → 3	587·5	587·5
	2 → 4	814·2	814·4
	3 → 5	1034·5	1034·6
0 → 1	0 → 0	Not resolved	4162·1
	1 → 1	4156·2	4156·0
	2 → 2	4143·0	4144·8
	3 → 3	4127·0	4126·9
	1 → 3	4714·5	4713·3

The agreement between the two sets of values is very satisfactory.

In order to get intensity and polarisation measurements which may be compared with the theory, it is no doubt necessary to work in the gaseous state at as low pressures as possible, thus minimising the uncertainties due to the mutual influence of molecules, etc. But from a practical point of view, one has to adopt fairly high pressures to obtain scattered light of reasonable intensity. The fact that the values given by Rasetti who worked with the gas at a pressure of 12 atmospheres agree so remarkably well with those obtained by the author at much higher pressures is a convincing proof that the frequencies are quite independent of pressure. Apart from such a constancy of the frequency shifts, it also appears that in hydrogen gas, neither the sharpness nor the intensities of the various lines are appreciably affected by moderately high pressures. The present writer has photographed the rotation lines at three different pressures, *viz.*, 13, 20 and 36 atmospheres with exposure time inversely proportional to the pressure employed. The lines as recorded remain perfectly sharp at all the three pressures and actually show a slight increase in intensity with increased pressures as may be expected from the fact that the Schwarzchild correction has not been taken into account in giving the different exposures. It is also significant that the frequency shifts recorded by McLennan, Smith and Wilhelm for the strong lines in liquid hydrogen agree very closely with the corresponding values given by Rasetti and by the author. Further, the rotational transitions appear in their photographs as quite sharp lines in spite of the fact that the density of the liquid is nearly 800 times as great as the density of the gas at N.T.P.

The above results are not surprising in view of the recent work of the present writer[6] on the effect of pressure on the rotational quantisation in gases. It was found with various gases that unless the pressure is so high that the frequency of molecular collisions approaches the frequency of rotation, the individual rotation lines are not appreciably affected either in sharpness or in intensity. A calculation was made of this *critical* pressure in several cases from considerations of viscosity, mean free path, etc., and good agreement shown to exist between these and the experimentally found pressures beyond which the rotation lines cease to be sharp. Owing to the low moment of inertia of the hydrogen molecule, this pressure comes out as 450 atmospheres. Thus there appear to be good reasons, both theoretical and experimental, for believing that pressures up to 50 atmospheres or even more could be used in the case of hydrogen without introducing any complications due to molecular collisions affecting the intensity or sharpness of the Raman lines.

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[6] Ind. Jour. Phys., *loc. cit.*

4. *Intensity of the Raman Lines in Hydrogen.*

It will be noted from Table I that the Raman frequencies recorded may be divided into three distinct groups, *viz.*, (*i*) six lines arising from changes in the rotational energy alone of the molecule, (*ii*) three close lines arising from changes in the vibrational energy alone of the molecule, (*iii*) one line arising from a simultaneous change in both the rotational and vibrational energies of the molecule. An experimental investigation of their relative intensities is of great importance and will form the subject matter of this section.

Rotation lines:—Fig. (*a*) in plate IX is obtained directly without any polariser in the path of the scattered beam and represents the total scattering, *i.e.*, a superposition of the vertical and the horizontal components. Fig. (*b*) is obtained after interposing a nicol with its vibration axis horizontal and is thus a record only of the weaker of the two principal components of all the lines. It is very clear from the pictures that the relative intensities of the various rotation lines remain quite the same in both cases. This is merely a consequence of the experimental fact, to be described later, that the individual rotation lines are all polarised to exactly the same extent.

Two independent methods have been adopted for measuring the relative intensities of these lines. In the first method, a series of photographs of the scattered spectrum are obtained on the same plate keeping the pressure of the gas, conditions of illumination and other details of the arrangement practically unchanged. The times of exposure are so adjusted that the lines which are being compared are recorded with equal densities. Under these conditions, the ratio of their intensities may easily be obtained from the relation

$$I_1/I_2=(T_2/T_1)^{0.86}$$

where I and T stand respectively for the intensity and time of exposure. In this way, the relative intensities of the various lines in Fig. *a* (total scattering) have been determined.

In the second method, a scale of intensity marks is obtained by varying the width of the spectroscope slit to known extents and exposing in each case for the same time the radiation from a standard tungsten ribbon lamp. The density at any desired wave-length is obtained for each of the intensity marks by running the plate through a Moll microphotometer and the corresponding intensities are taken as proportional to their respective slit widths. In this way, the density-log intensity curves are drawn for each wave-length at which the various rotation lines that are to be compared with each other appear. The scattered spectrum is exposed on another plate but is developed along with the above intensity marks in the same dish under identical conditions. A single microphotometric record of the various rotation lines (See plate VIII) enables the density of each of them to be determined, and the corresponding intensities as fractions of the standard radiation having the same wave length as the line itself may be read off from the above curves. The relative intensities may then be easily determined from a knowledge of the intensity distribution in the radiation emitted by the tungsten lamp. This method has been adopted for determining the relative intensities of the lines in Fig. *b* (horizontal components only). It may be noted that the results obtained in the second case are free from errors due to variations in the photographic sensitivity of the plate in different regions of the spectrum, and is in this way superior to the first method. The results are given in Table II.

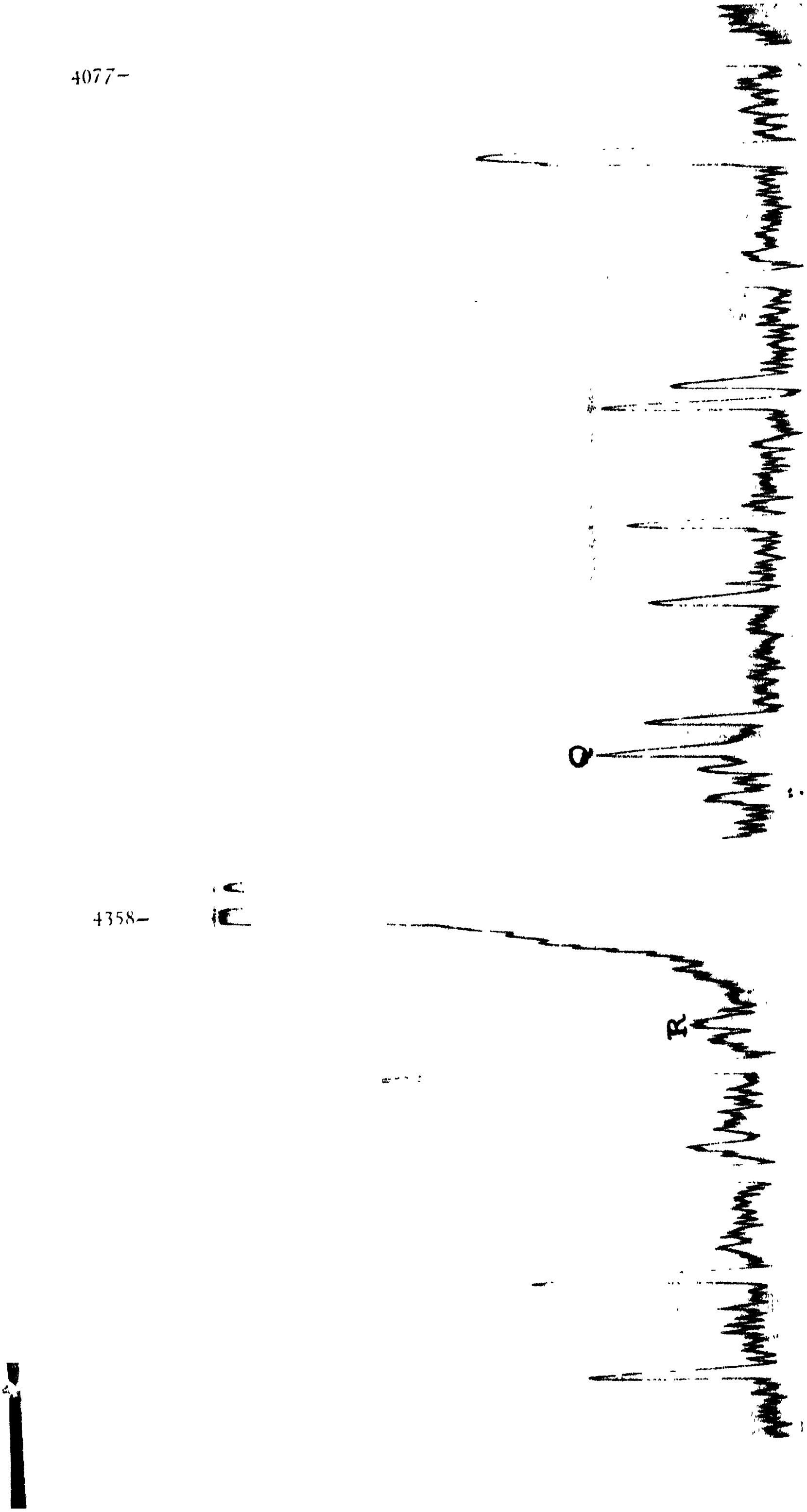
Table II

Relative intensities of rotation lines.

Transition.		Total scattering.	Horizontal component.
n.	K.		
0→0	3→1	0·15	0·13
	2→0	0·15	0·13
	0→2	0·7	0·67
	1→3	2·0	2·5
	2→4	0·3	0·30
	3→5	0·2	0·21

It will be seen that the agreement between the two sets of values is satisfactory. The marked discrepancy in the case of the intense 1→3 line is due to the fact that its density was so large that the corresponding intensity had to be derived from an extrapolated portion of the density-log intensity curve. The value in column two is therefore to be preferred for this line.

Vibration lines:—The next problem is to compare the intensities of the fine structure components of the vibrational



Microphotograph the zon component hydrogen spectrum

scattering. These are shown by three arrows in the microphotometric record reproduced in Plate X. All the three components are excited by λ3650 mercury radiation. The comparison is made only by the former of the above methods and the results are to be regarded as somewhat less accurate on account of the extreme closeness of the lines.

TABLE III.

Relative intensities of the fine structure components.

Transition $n : 0 \to 1$	K : $0 \to 0$	$1 \to 1$	$2 \to 2$	$3 \to 3$
Intensity of total scattering.	not resolved	5·0	0·8	0·8

Vibration and vibration-rotation lines :—In the case of pure rotation lines dealt with above, the various radiations which were being compared are all polarised to the same extent, and hence it was of no consequence whether the comparisons were made in the total scattering Fig. (*a*) or in the horizontal components alone Fig. (*b*) of Plate IX. The situation now is however quite different as the vibration lines are well polarised whereas the vibration-rotation lines are badly polarised. The two cases will lead to wholly different results. In the total scattering, the vibration line represented by $n : 0 \to 1$; K $: 1 \to 1$ has been compared with the vibration rotation line represented by $n : 0 \to 1$; K $: 1 \to 3$ by the time-exposure method, while in the horizontal component of the scattered light, these two lines are compared by the method of intensity marks. The latter course is adopted for the horizontal components with a view to get accurate values on account of the great theoretical significance of this result. These two lines are marked by the letters Q and R respectively in Figs. (*a*) and (*b*), Plate IX and also in the micro-photometric record of the horizontal components alone (plate VIII).

TABLE IV.

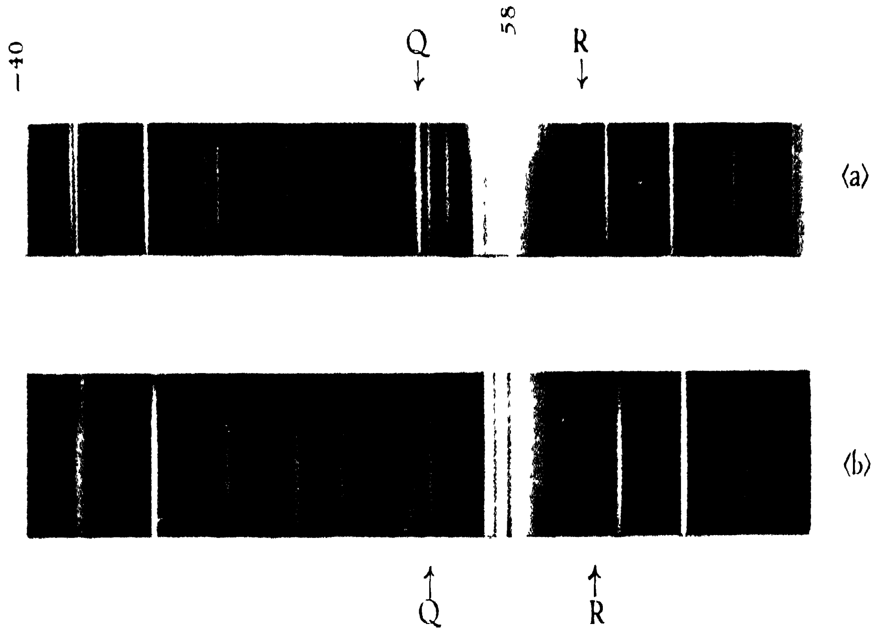
Relative intensities of vibration and vibration-rotation lines.

Transition		$n: 0 \rightarrow 1$ $K: 1 \rightarrow 1$	$n: 0 \rightarrow 1$ $K: 1 \rightarrow 3$
Intensity	Total Scattering	5·0	0·8
	Horizontal Components.	1·23	0·8

The remarkable fact that has to be noted is the larger intensity of the vibration line in comparison with the vibration-rotation line even in the horizontal component. This is clearly seen in the microphotometric record as well as the photograph of the spectrum itself reproduced in the present paper.

5. *Polarisation of the Raman Lines in Hydrogen.*

Method of measurement:—The scattered beam is made to pass through a suitably orientated nicol before it enters the spectrograph, and the horizontal and the vertical components are separately photographed side by side on the same photographic plate. In order to determine their relative intensities, use is made of the relation $(I_H/I_V = T_V/T_H)^{0{\cdot}86}$ where I and T represent respectively the intensity and the time of exposure. This relation holds good if the densities of the two images are equal. The two components should therefore be exposed for different times, the times being so adjusted by trial that the images are recorded with equal density on the plate. In practice, a series of photographs are taken of the vertical component along with one of the horizontal component providing a sufficiently close range of



(a) Total scattering, (b) Horizontal component.

Raman spectrum of hydrogen gas

depolarisation values.[1] By examining the pictures, it is easy to fix the limits for the depolarisation of the particular line under consideration.

Results:—In this manner, the depolarisations of two rotation lines and the principal vibration line are determined. The results are given in Table V.

TABLE V.

Depolarisation of Raman lines.

Transition.	K : 0 ⟶ 2	K : 1 ⟶ 3	K : 1 ⟶ 1 ; *n* : 0 ⟶ 1
Depolarisation.	0·85 ± 0·05	0·85 ± 0·05	0·16 ± 0·02

In the case of the vibration line given in the last column, the actual times for obtaining equality of the horizontal and the vertical components are in the ratio of 14 : 100. This ratio, *viz.*, 0·14 when corrected for, by introducing 0·86 in the power of time, becomes 0·184. The value is, however, given as 0·16, the diminution effected being a correction due to a lack of transversality in the incident beam as will be explained later. An independent but an approximate check on this value may be obtained from the results given in the foregoing section on the relative intensities of the various Raman lines. In Table IV, a comparison is made of the intensity of the vibration line (K : 1 ⟶ 1 ; *n* : 0 ⟶ 1) with that of the vibration-rotation line (K : 1 ⟶ 3 ; *n* : 0 ⟶ 1) for both total scattering and the horizontal components. It is clear from the two photographs reproduced in plate IX that the latter is depolarised to the same extent as the pure rotation lines. This may be seen by comparing it with the neighbouring rotation line 0 ⟶ 2 in both the photographs. The result is in accordance with what we should expect from the theory, and thus taking the depolarisation of the vibration-rotation line to be also 0·85, we can easily calculate the state of polarisation of the principal vibration line from the figures given in Table IV. The result comes out as 0·13 in reasonable agreement with the directly determined value. The small discrepancy is probably due to the inaccuracy in the intensity measurements by the time exposure method.

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[1] Depolarisation is defined in the usual way as I_H / I_V.

An outstanding feature in the results of this section is the large depolarisation exhibited by the rotation and vibration-rotation lines as contrasted with the strong polarisation of the vibration line. The depolarisation of the individual rotation lines is in close agreement with the theoretical deductions of Manneback. The significance of the depolarisation value for the vibration line will be dealt with in a later section on the discussion of the results.

6. *Sources of Error and the Necessary Corrections.*

In the above method of measurement, there are various sources of error which one has to guard against. Mention has already been made of some of these and the necessary corrections, in earlier communications by the present writer dealing with the subject of polarisation of Raman lines in liquids. Apart from such errors, there are also others which are peculiar to the present work on gases, and a comprehensive discussion will be given here of the various corrections employed and the tests made in order to render the results free from such uncertainties.

(*a*) *Polarisation due to oblique refraction at the prism surfaces* :—In accordance with the well-known Fresnel's laws of reflection and refraction, the horizontal and the vertical components are in general neither reflected nor transmitted equally by transparent media. As a result, the depolarisation of any radiation passing obliquely through the prisms of the spectrograph is altered: the vertical component loses more than the horizontal one and the depolarisation is apparently enhanced. The error introduced in this manner is, however, a constant characteristic of the instrument used and may be determined very exactly by allowing unpolarised light to fall on the slit of the spectrograph and determining its state of polarisation as it emerges out at the other end. The corresponding correction is introduced in the times of exposure for the horizontal and the vertical components.

(b) *Lack of transversality in the incident beam* :—It is well-known that when unpolarised incident light is used, the depolarisation of the scattered light is a minimum in the transverse direction and goes on increasing on its either side with increasing obliquity till it becomes completely unpolarised in directions which are parallel to that of the propagation of the incident beam. Thus, it appears necessary that in order to obtain experimentally the true depolarisation (*i.e.*) the depolarisation in the transverse direction, one has to use a strictly parallel incident beam and make the observation at an angle of 90° with it. In practice, matters are, however, somewhat simpler, as it was shown by I. R. Rao[7] that the use of a condenser for focussing a source of light of small angular aperture introduces no error under this head so long as observation of the scattered light is made at the exact focus. The source used in the present experiments is, however, an extended one being a quartz mercury arc of 6 inches length and is likely to introduce a certain error under this head. The error will however be relatively more serious in the case of low depolarisation values than in the case of the higher depolarisations. In the case of the rotation lines which are very nearly unpolarised even in the transverse scattering, this correction may altogether be neglected. The vibration line, being a well polarised line, stands on a slightly different footing. In order to get an idea of the magnitude of the correction necessary, a computation is made in the following way. If ρ is the true depolarisation for strictly transverse scattering when unpolarised incident light is used, ρ_θ, the depolarisation of the beam scattered at a direction θ from the transverse case, is given by the relation

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[7] Ind. Jour. Phys., 2, 61 (1927).

$$\rho_\theta = \rho + \sin^2\theta(1-\rho)$$

The average value of this function may easily be obtained by integrating it between the limits $\pm\alpha$ where α is the extreme angle at which rays are likely to enter the gas tube from the condenser under the conditions of the experiment. For a column of 5 inches of illuminated gas kept at a distance of about 8 inches from the condenser, the average value of the correction factor $\sin^2\theta(1-\rho)$ comes out as $+0{\cdot}026$ in the neighbourhood of $\rho = 0{\cdot}15$. The magnitude of the correction varies very little with varying values of ρ.

The results of the above computations are independently checked by the following experiment. A tube of liquid carbon tetrachloride is illuminated under conditions exactly similar to those used in the experiments with the hydrogen gas, illuminated column being about 5 inches in both cases, and the state of polarisation of the Rayleigh scattering mixed with the accompanying rotational Raman scattering is determined opening the slit of the spectrograph wide. The experiment is repeated with a mercury point source* and also using sunlight, the depolarisation in the latter case being determined visually by the Cornu method. The results are given in Table VI.

TABLE VI.

Depolarisation of Rayleigh scattering in CCl_4.

Sunlight.	Mercury Point-source.	6 inch mercury arc.
0·049	0·045	0·076

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* Details regarding this lamp are given in a later section. The length of the arc is only about 1 mm. and the method is therefore free from any errors due to lack of transversality.

The slight discrepancy between the visually obtained sunlight value and the spectroscopically obtained mercury point-source value is probably due to the presence of some nearly unpolarised vibration lines of appreciable intensity in the scattering by CCl_4. The use of a 6 inch mercury arc on the other hand has only increased the value by about 0·03 in good agreement with the foregoing computations of the magnitude of this error.

(*c*) *Photo-elastic effect in the observation window* :—It is absolutely necessary that in the course of the exposures for both the horizontal and vertical components, the pressure in the gas tube should remain constant. Such a perfect freedom from leakage can only be obtained by putting a considerable amount of pressure on the glass plate G between the rubber washers (fig. 1) by means of the screw cap. Although, the presence of thick rubber washers tends to render the strain on the glass plate quite uniform, there is a certain chance of the window developing a photo-elastic effect under strain. In order to test this point, nitrogen gas was put into the tube at a pressure of about 45 atmospheres and its depolarisation determined visually using sunlight. The value obtained is 0·041 in fairly good agreement with the value determined in an apparatus with unstrained window at atmospheric pressure, *viz.*, 0·036. The discrepancy of 0·005 may be due either to a small strain in the window or to a minute quantity of dust floating in the gas. This, however, is negligible in comparison with the depolarisation values of the various Raman lines as even the vibration line which is the best polarised exhibits a depolarisation about thirty times as large as this quantity.

7. *Rayleigh Scattering by Hydrogen.*

Experimental technique :—The apparatus described in the foregoing pages has the disadvantage that the parasitic light is not completely eliminated, though it may be diminished relatively to the genuine scattering, by covering up a portion of the illuminated length of the tube. If we are interested in investigating the intensity and polarisation characters of the Rayleigh scattering, it is very essential that the parasitic light should be reduced to an absolute minimum even at the cost of diminishing the intensity of scattering to some extent. In order to suit this part of the work, a special form of apparatus has been constructed, the details of which are given below. It is shown diagrammatically in Fig. 2.

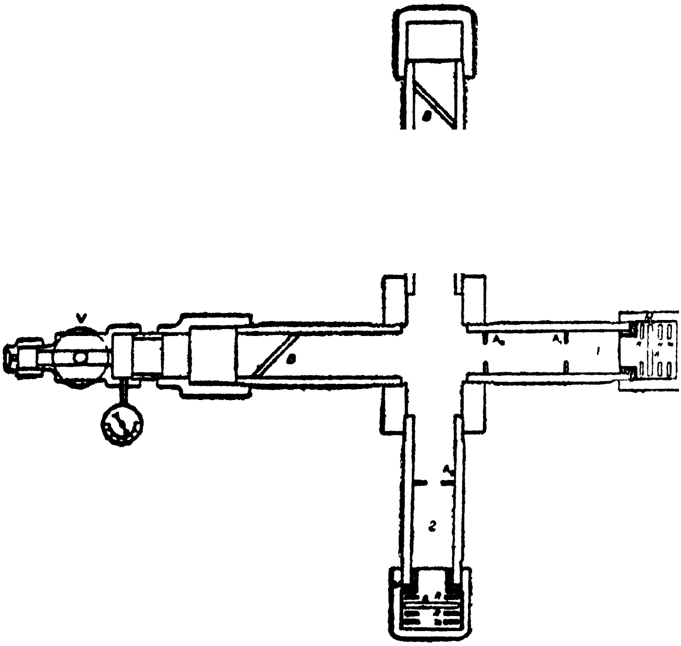

Fig. 2.

Four strong steel tubes are screwed on to a rectangular steel chamber in which two holes are drilled at right angles to each other. They serve to connect the two pairs of opposite tubes making the apparatus resemble a hollow cross. Light enters through steel tube 1 and passes off into the opposite tube without striking any of the walls, and is absorbed by a suitably placed black glass at the other end. The scattered light emerges out through the tube 2 and is taken into the spectrograph. Opposite the observation tube is another inclined black glass B so that any light that may get to the back by reflection at the walls is partly absorbed and partly reflected *away* from the slit of the spectograph. Tubes 1 and 2 are provided with glass windows $\frac{3}{8}$ inch thick for the entry and exit of the light. These are held between thick rubber washers to prevent leakage of gas. In the figure, the glass window is indicated by G, rubber washers by R and an iron washer by m. All these are contained in a metallic ring M, the purpose of which is partly to prevent spreading out of the rubber when squeezed, and are screwed on to the steel tube by a nut of suitable size. Two apertures A_1 and A_2 in the tube through which the incident light passes and one A_3 in the observation tube serve the very useful purpose of preventing the light from falling directly on the walls of the steel chamber thus giving rise to parasitic light. In addition to the above precautions, the inside of the apparatus is blackened by means of a non-glossy paint. The gas is admitted through a pin valve V after evacuating the whole apparatus and the pressure is read on a gauge attached to the pin-valve. Pressures up to 75 atmospheres could be used in this apparatus.

It is obvious from figure 2 that the usual type of a long mercury arc is unsuitable in conjunction with this apparatus. A special mercury point lamp in which the arc strikes between a thick tungsten anode and a mercury surface serving as the cathode is used. A steady current of 2 amperes at a terminal voltage of about 11 to 12 volts is maintained by means of suitable resistances. Under these conditions, the length of the arc does not exceed about 1mm. and it runs continuously without any attention. A slightly higher current could also be sent (about $2\frac{1}{2}$ amps.) if the anode is cooled by water slowly dripping on to it, resulting in a larger intensity. The light from this point source is focussed into the centre of the steel chamber shown in Fig. 2 by means of a lens. Such an arrangement, besides eliminating the errors due to lack of transversality in the scattered beam, very effectively eliminates the parasitic light if sufficient care is taken to focus the beam in such a way that it does not strike the walls of the container vessel.

Results:—Adopting the above arrangements, the ratio of intensities of the horizontal components of the Rayleigh scattering and the rotation line corresponding to 1—>3 transiton have been determined by the method of intensity marks. In Table VII, the relative intensities obtained are given after applying the necessary corrections described below. It is to be noted that the Rayleigh scattering (Q branch) is much stronger than the rotation line 1—>3 (R branch). The latter is shown by an arrow in Fig. b of Plate X.

TABLE VII.

Relative intensities of Rayleigh and rotation lines.

Horizontal component Rayleigh scattering.	Horizontal component rotation line K : 1—>3
2·3	1·0

8. *Sources of Error and the Necessary Corrections.*

(a) *Parasitic light*:—This tends to intensify the Q branch of the Rayleigh scattering and when comparing only the horizontal components as in the above case, even minute traces of parasitic light become relatively appreciable on account of the extreme feebleness of scattering. The amount of parasitic light has therefore, to be determined and corrected for. This is done by evacuating the gas tube *in situ* and giving an equal exposure with the evacuated tube on the same plate on which the Rayleigh scattering is recorded (See fig. a of plate X). The intensity thus obtained is then subracted from the recorded Rayleigh scattering in order to arrive at the magnitude of the true Rayleigh scattering.

(*b*) *Photo-elasticity of the glass windows.*—The significance of this is already discussed in connection with the other apparatus. Separate tests have been carried out with the present cross apparatus in order to see if the observation window has developed any possible non-uniform strain. Table VIII contains the measurements of depolarisation for CO_2 and H_2 at different pressures obtained visually by the Cornu method using sunlight.

TABLE VIII.

Depolarisation of the scattered light in CO_2 *and* H_2

Gas	Carbon dioxide		Hydrogen	
Pressure in atmospheres.	15	10	70	50
Depolarisation	0·094	0·094	0·033	0·031

The reading in the last column was taken without changing the pressure on the windows, that is immediately after photographing the Rayleigh scattering. Others were obtained on different occasions. The agreement between them and the values obtained for these gases with strain—free windows at atmospheric pressures, *viz.*, 0·098 for CO_2 and 0·032 for H_2 clearly shows that the window is in general quite free from any effect due to photo-elasticity.

(*c*) *Presence of dust.*— If there is any dust floating in the gas, the light scattered by those particles tends to increase the depolarisation and will lead to serious errors when computing the relative intensity of the horizontal component of the Rayleigh scattering. In practice, it is found that if the apparatus is allowed to rest for a period of about 3 to 4 hours after filling in the gas, all the floating particles settle down on the walls of the vessel and the illuminated part of the gas is quite free from dust. The above readings have been obtained in this manner. In order, therefore, to eliminate this source of error, the exposure is begun only after allowing the apparatus to rest in its place, after making the adjustment, for a period of 20 to 24 hours. Under such conditions, the scattering is wholly molecular and no correction need be made under this head.

(*d*) *Presence of other gases as impurities.*—It may be noted that the average value of depolarisation given for hydrozen, *viz.*, 0·032 obtained with this apparatus by using sunlight and high pressure, although in agreement with the values obtained with the same sample of gas at atmospheric pressures, is a little higher than the actual depolarisation of scattering by pure hydrogen which is only 0·027. The discrepancy is presumably due to the fact that there is a certain percentage of impurity of oxygen. In order to test the purity of the gas, a few density determinations have been carried out, the average of the readings reduced to N.T.P. being 0·000120 gms. per c.c. The density of a sample having a 2% impurity of oxygen works out as 0·000118 gms. per c.c. in close agreement with the experimental value. This amount of impurity is also just sufficient to account for the rise of depolarisation of hydrogen from 0·027 to 0·032. On the other hand, the same increase of depolarisation could as well have been accounted for by a much larger percentage impurity of nitrogen but the assumption would be totally inconsistent with the density determinations. Thus, the depolarisation measurements when supplemented with the density determinations definitely indicate that the impurity is about 2% of oxygen, and an appropriate correction has to be applied for obtaining the true intensity of scattering from hydrogen as itself.

9. *Discussion of the Results.*

A theory based on quantum mechanics for the intensity and polarisation phenomena in Raman scattering by diatomic molecules has been given by Manneback, and a comparison of its essential features with experimental facts is best made for the simplest molecule, *viz.*, H_2. It will be seen in the following pages that most of the experimental results are in beautiful agreement with the theoretical predictions, thus affording for the first time a convincing proof of the essential correctness of the ideas underlying this notable work regarding the mechanism of the production of Raman radiations. There are, however, certain very significant differences whose implications appear to have far-reaching consequences. A comprehensive discussion will now be presented of the theory and its relation to the experimental facts already described.

Rasetti has already shown that, in order to account satisfactorily for the observed rotation frequencies, we have to take the value of $B_0 = h/8\pi^2 I_0 c$ to be $59{\cdot}40 \pm 0{\cdot}03$. I_0 stands for the moment of inertia of the molecule in the normal state and assumes a value $0{\cdot}466 \times 10^{-40}$. Other letters have the usual significance.

Polarisation of individual rotation lines.—Manneback deduced that every line arising from a rotational transition should be depolarised to the extent of 3/4 if plane polarised incident light is used and to the extent of 6/7 if unpolarised incident light is used. This result is independent of temperature and is capable of exact verification. Results given in Table V are in complete agreement with this conclusion. Reference may also be made here to the results of the classical theory in this respect. [8]

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[8] S. Bhagavantam, Ind. Jour. Phys., 6, 331 (1931).

Relative intensities of the various rotation lines.—The relative intensities of the various rotation lines K⟶K±2 can easily be obtained from the fomulae

$$I_{K\rightarrow K+2} \propto S(2K+1)e^{-\sigma K(K+1)} \cdot \frac{(K+1)(K+2)}{(2K+3)(2K+1)}$$

$$_{K\rightarrow K-2} \propto S(2K+1)e^{-\sigma K(K+1)} \cdot \frac{(K-1)k}{(2K-1)(2K+1)}$$

In the above expressions $S=1$ if K is even and $S=3$ if K is odd on account of the different *a priori* probabilities for the symmetrical and antisymmetrical states. $\sigma=B_0ch/kT$ where T is the absolute temperature and k the Boltzmann constant. The expressions do not include a small and very minor correction due to the ν^4 law for the intensity of the scattered radiation. Taking B_0 to be equal to 59·40 as explained above, the relative intensities calculated for the rotation lines at a temperature of 30°C are given in Table IX along with the observed values.*

TABLE IX.

Relative intensities of rotation lines.

Transition	P series.		Transition	R series	
	Calculated	Observed		Calculated	Observed
2⟶0	0·124	0·13	0⟶2	0·666	0·67
3⟶1	0·124	0·13	1⟶3	2·053	2·0
4⟶2	0·006	—	2⟶4	0·318	0·30
			3⟶5	0·229	0·21
			4⟶6	0·0098	—

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* Manneback has also carried out the numerical computations for a temperature of −14°C. This has been given as 14°C owing to misprint in his paper. The room temperature in India is about 30°C and hence the calculations are repeated here.

It will be noted from the Table that the agreement is very satisfactory. The relatively low intensity of the lines in the P series in comparison with the R series is a special feature of the quantum theory which is confirmed by experiment. Since it arises from the presence of Boltzmann factor in the expression for the intensity, it may be referred to as a "temperature dissymmetry" of the rotational Raman spectrum, and is specially prominent in the case of hydrogen owing to the low moment of inertia of the molecule. The calculations clearly show that the intensity rapidly falls off with increasing quantum numbers, and in order to photograph either the 4⟶2 or the 4⟶6 line, one would have had to expose the picture for about 20 times the normal period. The non-appearance of these lines in the photographs obtained by Rasetti in the ultra-violet and by the present writer in the visible region of the spectrum is thus fully explained.

Relative intensities of the fine structure components of the vibration line.—These components are closely spaced lines arising from the fact that the vibrating molecules have slightly different frequencies if they belong to different rotational states. Three of these components are shown by arrow marks in the vibration line excited by λ 3650 (see microphotometric record in Plate X). According to the theory developed by Manneback, the intensity of a vibration line is a function of two quantities, *viz.*, the variations caused of the polarisability and optical anisotropy of the molecule by a change in the nuclear distance, and is sensibly independent of the rotational state of the molecule, so long as its rotational energy is unaltered in the transition. Thus, the relative intensities of the lines specified by the quantum transitions $n:0 \longrightarrow 1$ and $K:0 \longrightarrow 0$, $1 \longrightarrow 1$, $2 \longrightarrow 2$ and $3 \longrightarrow 3$ respectively may be taken as proportional to the relative populations of the molecules in the 0, 1, 2, and 3 rotational states. The relative number of

$$N_K = S(2K+1)\, e^{-\sigma K(K+1)}$$

molecules in each state is easily calculated by the relation where S as before is equal to 1 if K is even and 3 if K is odd. Other letters have the usual significance. The calculated results are compared with the observed intensities in Table X.

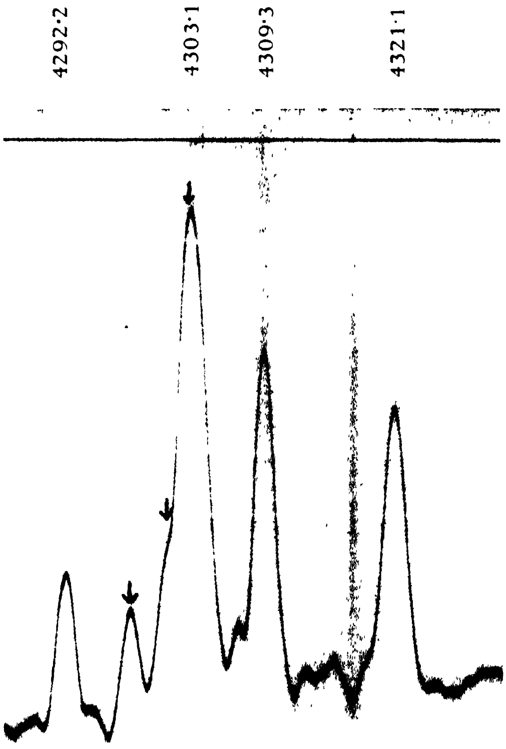
TABLE X.

Relative intensities of the fine structure components.

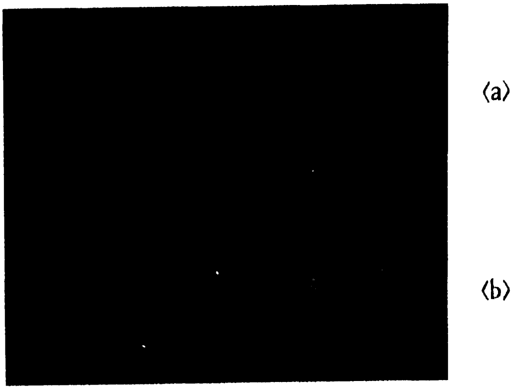
Transition $n: 0 \rightarrow 1$	$K: 0 \rightarrow 0$	$1 \rightarrow 1$	$2 \rightarrow 2$	$3 \rightarrow 3$
Calculated	1·00	5·13	0·93	0·72
Observed	not resolved	5	0·8	0·8

This method of calculation is however only approximate and in the rigorous theory developed by Manneback, slight deviations from the above proportionality to the thermal distribution are to be expected. This consequence is intimately connected with another interesting result, implied in Manneback's theory of the fine structure components, according to which we should expect the first component, *viz.*, $n: 0 \rightarrow 1$; $K: 0 \rightarrow 0$ to be perfectly polarised while the higher ones corresponding to K : $1 \rightarrow 1$, $2 \rightarrow 2$, $3 \rightarrow 3$, etc., exhibit gradually increasing depolarisation values. These points are under investigation by the author using suitable dispersion and the results will be dealt with in a later communication.

Relative intensity of the Q and R branches.—The Rayleigh or undisplaced line in the spectrum may be designated as a Q branch, accompanying which are the rotational lines $K \rightarrow K+2$ and $K \rightarrow K-2$ forming the R and P branches respectively. Manneback's theory gives a relation connecting the *intensity* of the three branches for the case of a diatomic molecule which is most elegantly expressed by saying that the intensity of the Q branch, considering the horizontal or



Fine structure components of the vibration line in H_2.



Wide slit spectrogram of the horizontal component in the scattering by H_2: comparison of Q and R branches.

weaker component only, is 1/3 the aggregate intensity of the horizontal components of all the lines in the P and R branches. In the case of hydrogen, however, we are concerned with the intensity of the *individual* lines in the P and R branches which are accessible to direct observation. We may choose the most intense of these lines, *viz.*, the one in the R branch corresponding to the transition 1⟶3 and compare it with the Q branch. The latter arises from molecules distributed according to the Boltzmann law over a range of rotational states designated by the quantum numbers 0, 1, 2, etc., and represents the composite or superposed effect of all such molecules. The intensities of these two lines are proportional to the expressions given below. The horizontal and the vertical components are given separately. μ is the average polarisability of the molecule and γ is the optical anisotropy defined as the difference between the two principal polarisabilities. The expressions are valid only if incident plane polarised light is used.

	Q branch (aggregate)	R branch line K : 1⟶3
Vertical component	$E^2\left(\mu^2+\frac{1}{45}\gamma^2\right)$	$\dfrac{12/25\ E^2\gamma^2 e^{-2\sigma}}{\sum\limits_{K=0}^{\infty}(2K+1)e^{-\sigma K(K+1)}}$
Horizontal component	$E^2\gamma^2\frac{1}{60}$	$\dfrac{9/25\ E^2\gamma^2 e^{-2\sigma}}{\sum\limits_{K=0}^{\infty}(2K+1)\,e^{-\sigma K(K+1)}}$

In the case of unpolarised light, each of the vertical components will be increased by an amount equal to the corresponding horizontal component and the horizontal components themselves will be doubled. It is easily seen from the expressions that if we are interested in comparing the horizontal components amongst themselves, γ the optical anisotropy of the molecule is automatically eliminated and the comparison becomes very simple. The situation regarding the Q branch of the vibration scattering is, however, somewhat different, as the various vibration lines coming from molecules possessing different rotational energies are separated from one another (see microphotometric record in Plate X) and we are no longer justified in talking about the superposed intensity of the Q branch. We shall concern ourselves with the most intense line having the quantum designation $n: 0 \longrightarrow 1$; $K: 1 \longrightarrow 1$ represented by the highest peak in the microphotometric record referred to above and by the letter Q in figs. *a* and *b* of Plate IX and compare its intensity with the vibration-rotation line $n: 0 \longrightarrow 1$; $K: 1 \longrightarrow 3$ marked by R in the same photographs. According to Manneback's theory, their respective intensities are proportional to the following expressions:—

Transition	$n: 0 \longrightarrow 1; K: 1 \longrightarrow 1$	$N: 0 \longrightarrow 1; K: 1 \longrightarrow 3$
Vertical component	$3E^2(\mu'^2 + 8/225\gamma'^2)e^{-2\sigma}$	$4/25E^2 \gamma'^2 e^{-2\sigma}$
Horizontal component	$2/45E^2\gamma'^2 e^{-2\sigma}$	$3\ 25E^2 \gamma'^2 e^{-2\sigma}$

As before the vertical and horizontal components are given separately and the expressions are valid only for plane polarised incident light. In the case of unpolarised light, each vertical component should be increased by an amount equal to the corresponding horizontal component and the horizontal components themselves should be doubled. Instead of μ and γ we now have μ' and γ' which are related to μ and γ in the following way:—

$$\mu' = x\sqrt{\tfrac{1}{2}}\,R_o\,(d\mu/dR_o)$$

$$\gamma' = x\sqrt{\tfrac{1}{2}}\,R_o\,(d\gamma/dR_o)$$

where R_0 is the nuclear distance of the molecule in the equilibrium position. While comparing the horizontal components alone, γ' is eliminated as before and the ratio comes out in terms of simple numbers as 10 : 27. On the other hand, a comparison of the two lines in the total scattering involves a knowledge of μ' which appears only in the expression for the vertical component of the Q branch. The total value of this term in relation to the horizontal component may, however, be evaluated from a knowledge of the state of polarisation of the Q branch (see Table V). In this way, their relative intensities in the total scattering are calculated and given along with the observed values in Table XI. It will be noticed that there is a striking disagreement between the observed and calculated results in both cases.

TABLE XI.

Relative intensities of the Q branch and the R branch rotation line $K: 1 \rightarrow 3$.

	Q branch observed.	R branch.		
		$K:1\rightarrow 3$ observed.	$K:1\rightarrow 3$ Calculated according to Manneback.	$K:1\rightarrow$ Calculated according to spinning photon theory.
Rayleigh scattering horizontal component.	2·3	1·0	3·61	1·82
Vibration scattering horizontal component.	1·23	0·8	3·32	0·71
Vibration scattering total.	5·0	0·8	4·01	0·86

Theory of the spinning photon.—Attention must be drawn here to the significant fact that while the theory developed by Manneback accounts very satisfactorily for the relative intensities of the various rotation lines constituting the P and R branches, it presents a sharp conflict with the experimental results when we compare any of these lines with the intensity of the Q branch itself. This suggests that something fundamental to the calculations has been omitted in computing the intensities of all the rotation lines. The necessary modifications of the theory have already been indicated in a preliminary communication[9] and are based on the view that the possession of an angular momentum $\pm h/2\pi$ by the light quantum has not adequately been taken account of in the theory of scattering by diatomic molecules. The following essential ideas underlying the modified theory will make clear the procedure adopted in obtaining the new results.

If we regard radiation, impinging on a rotating molecule, as a particle possessing an intrinsic spin $\pm h/2\pi$ and the result of such an encounter as obeying the law of conservation of angular momentum, the sense of spin which the molecule possesses in relation to that of the photon should obviously enter into the problem in a fundamental way. In the existing theories of radiation, on the other hand, the sense of spin of a linearly polarised photon is conceived of as indeterminate and in any encounter, the photon has an equal chance of increasing or diminishing the rotational energy of the molecule : the sense of rotation of the molecule is of no consequence. In the theory of spinning photons, if we consider the various possibilities of the relative orientations of the molecule spin* and the photon spin, it will be easily seen that in half the number of possible encounters, the exchange of rotational energy is forbidden while in the other half it is allowed. It is further assumed that if an encounter is one in which the exchange of rotational energy is forbidden, then the light quantum is scattered as such without any change in its frequency and only adds to the intensity of the incoherent part of the Rayleigh scattering.

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[9] C. V. Raman and S. Bhagavantam, Ind. Jour. Phys., 6, 353 (1931).

* In the case of hydrogen molecules belonging to the zero quantum state, a possession of zero point angular momentum may be assumed.

In accordance with the foregoing views, we must transfer half the intensity of each one of the individual lines of the P and R branches to the composite Q branch in the Rayleigh scattering or to the corresponding fine structure component of the Q branch in the case of vibrational scattering. The figures in the last column of Table XI are calculated in this manner and exhibit satisfactory agreement with the experimental results. It will be noted that the two theories lead to very different results; in one case the R branch line is expected to be much stronger than the Q branch whereas in the other the situation is just the reverse, for the horizontal components. The fact that the Q branch is really stronger than the rotation line may be directly verified from the photograph reproduced in Fig. b of plate IX and its microphotometric record in plate VIII for the vibration scattering and Fig. b of plate X for the Rayleigh scattering.

In conclusion, the author desires to express his grateful thanks to Prof. Sir C. V. Raman for his kind criticism and helpful guidance.

TABLE XII.

Raman spectrum of hydrogen.

Wave-length.	Approximate Relative intensity (Horizontal components).	Exciting Line.	Quantum transition.	
			K	*n*
4105·4	3	4046	0→2	
4137·6	½	4077	0→2	
4145·0	10	4046	1→3	
4177·9	1½	4077	1→3	
4184·3	2	4046	2→4	
4217·7	½	4077	2→4	
4223·4	2	4046	3→5	
4249·6	2	4358	3→1	
4292·2	2	,,	2→0	
4297·7	½	3650	3→3	0→1
4300·6	½	,,	2→2	0→1
4503·1 Q	2½	,,	1→1	0→1
4309·3	1	3654	1→1	0→1
4321·1	1	3663	1→1	0→1
4409·1 R	1	3650	1→3	0→1
4415·6	½	3654	1→3	0→1
		4347	0→2	
4426·8	3	4358	0→2	
4453·1	½	4339	1→3	
4462·0	1	4347	1→3	
4472·9	10	4358	1→3	
4518·9	2	,,	2→4	
4564·4	2	,,	3→5	

13

Light-Scattering in relation to Molecular Structure : New Data for Depolarisation in 39 Gases

By

S. Parthasarathy.

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Abstract.

The paper describes the determinations of light-scattering for 39 gases made visually using sunlight. Argon shows a definite depolarisation of 0·56%. The upper limit for the depolarisation in helium given by Lord Rayleigh as 6·5% has been lowered to 3%. SiF_4 and $SiCl_4$ give the depolarisations of 3·11% and 1·64% respectively. Comparing these with the values 1·14% for CH_4 and 0·62% for CCl_4, it would seem that for the molecules of the RX_4 type, with increasing size of the X atoms, the anisotropy decreases, and with increasing size of the R atoms, the anisotropy increases. Polar groups have marked influence ; the positive groups, OH and NH_2, entering into a hydrocarbon, seem to lower the depolarisation, while the negative radical Cl enhances it. Ethane, ethylene and acetylene show progressive increase of anisotropy, as we should expect from the theory of Ramanathan, with diminishing nuclear distance between the carbon atoms. In the series CH_4, CH_3Cl, CH_2Cl_2, $CHCl_3$ and CCl_4, there is a regular increase of depolarisation followed by a diminution, the maximum being shown by CH_2Cl_2 with the lowest value for CCl_4. In the series HCl, HBr and HI, the depolarisation increases, being 0·71, 0·84 and 1·27 respectively for the above three gases. The depolarisation for the polar compound COS is less than that either for CO_2 or CS_2. For CO, we have only 1·30, and for NO only 2·68, both very small in comparison with 9·72 for CO_2 and 12·47 for N_2O.

1. *Introduction.*

It is a matter of common knowledge that the light scattered by gaseous molecules in a direction perpendicular to the incident beam is always imperfectly polarised. The late Lord Rayleigh[1] and Born[2] attribute this essentially to the optical anisotropy of the molecules, the polarisation induced in the molecule being dependent on its orientation with respect to the electric vector in the incident beam. Following up the suggestion of Sir C. V. Raman[3] that this anisotropy, as revealed by the depolarisation, is due mostly to the mutual action of the doublets induced in the various atoms of a molecule by the incident beam, Ramanathan[4] has worked out the connection between the optical anisotropy and the structure of the molecules. It is difficult, however, to understand why spherical atoms like those of argon, or tetrahedral molecules like those of methane and carbon tetrachloride should exhibit an optical anisotropy as indicated by the depolarisation of scattered light. It was with a view to examining the data more closely, and if possible, to find an explanation for the observed anisotropy that the present work was undertaken. Incidentally, some gases and vapours which are quite simple and, therefore, very interesting from the point of light-scattering have also been investigated. Many inorganic gases, not hitherto examined, are also included.

2. *Experimental Arrangements.*

Sunlight was focussed by a lens into the cross-tube containing the gas for observation. The cross-tube used was of metal, about $2\frac{1}{2}''$ in diameter with a thin coating of black enamel inside. Suitable diaphragms placed inside it served to cut off extraneous light other than the incident beam. Three of the four arms were about 10″ in length, with the fourth, opposite the observation arm, much longer and ending conically as in the previous investigations of Raman and Rao,[5] and I. R. Rao,[6] so as to give a perfectly black background. Thick glass plates were attached to the ends of the arm with sealing wax, and the two tubes for entrance and exit of the gas were fitted with stop-cocks. The whole apparatus was made quite leak-tight. For some observations, a pear-shaped glass bulb like the one used by Rao, put inside a cross with diaphragms, was used. Since the cross with such stuck-on glass plates will not stand much pressure, all the observations were carried out at a pressure of one atmosphere. It is an undoubted fact that, wherever possible, visual observations are much superior to photographic methods enabling one to detect cloud formation or dust particles, two very serious sources of error in such work which would affect the results considerably.

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[1] Phil. Mag., Vol. 35, p. 373 (1918); Scientific Papers, Vol. VI.

[2] Born ' Verh. Deutsch. Phys. Gesell,' Vol. 20, p. 16 (1918).

[3] Nature, Vol. 114, p. 49, (1924).

[4] Proc. Roy. Soc., A, 107, 684 (1925) and A 110, p. 123 (1926).

The difficulty of observing scattered light of feeble intensity is overcome by using sunlight as the incident radiation, and having the observer's eye in a sensitive state after resting for an hour or so in complete darkness. A large wooden cabin with fan and ventilators, admitting no light inside, was found to be suitable for this purpose as the observation chamber. A hole in one side admits the one arm of the cross, against which is placed a double image prism and a nicol carrying a graduated scale. The ratio of the intensities of the weak to the strong component gives the depolarisation factor *r*.

3. *Adjustments.*

There are some important adjustments which must be looked into to get the most accurate results.

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[5] Phil. Trans., 46, p. 483, (1928.)

[6] Ind. Jour. Phys., 2, p. 67, (1927-28.)

1. The most important of these is the exact normality of the observation to the incident beam. This is secured by setting the arms of the cross at right angles to each other and putting suitable diaphragms inside, so that all extraneous light is carefully excluded. Even within the observation tube, such apertures are placed when the illumination of the inside chamber is avoided.

2. The background should be perfectly dark. Otherwise, even though the two images of the track are against the same background, it would seem impossible to get below certain values without serious error. For substances with low depolarisation, such measurements will be wholly untrustworthy. To secure perfectly dark background, a conical-shaped bottle with its neck broken off is fixed to the usually longer arm of the cross, and then a black glass plate fixed to it at an angle. The whole cross is also painted black inside.

3. The track of light must be exactly horizontal. This is secured by setting the cross horizontal with a spirit level.

4. The observation should be made exactly at the focus. A little way either side, the beam being either convergent or divergent, will give depolarisation not at exact normality, but at an angle greater or less than 90°, which of course gives greater depolarisation.[7] For this, sunlight focussed by a lens of 12″ focal length and 3″ in diameter gave good and concordant results.

5. In using the double image prism, it is found to be of advantage to have the images one above the other and near enough, rather than either side by side or too far apart. Comparison is better made only when they are near together but separated. It is also essential that the two images should be exactly one above the other; that is, the principal directions of vibration in the double image prism should be exactly vertical and horizontal. To secure the vertical position, a

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[7] A. S. Ganesan, Phys. Rev., 23, 63 (1924).

distant plumb line is viewed through the double image prism, rotating it on its own axis when for the correct position the two images fall exactly one over the other.

4. *Preparation of Gases.*

Of utmost importance in the scattering experiment, is the fact that the gases and vapours should be quite free from dust particles. This is secured by passing the gases through tubes packed tightly with cotton wool and then into the cross, very slowly. Otherwise, the values are liable to serious errors, often increasing the depolarisation values.

Absolute freedom from moisture is no less important. A trace of it in many gases, produces clouds, the two images as seen through the double image prism being of differrent colours; scattering from such clouds, therefore, can be distinguished from pure molecular scattering. In such cases, the depolarisation factor decreases.

In many cases, it was found necessary to cut off all the active rays to prevent the chemical action of light, by suitable filters. A solution of quinine sulphate was effective in many cases, but in the case of sulphur dioxide, none was suitable. A black paper covered completely that end of the cross through which light was admitted and removed only momentarily at the time of observation while all the time a slow flow of the gas was kept up. Only a few observations could be made which were consistent. With hydrogen bromide and hydrogen idoide both the filter and the paper were used.

Perfectly dry gases, tried in this experiment, were not found to act on the enamel inside. In one or two cases it was found necessary to heat the cross so that the vapour might not condense on the sides.

Oxygen, carbon dioxide, ammonia, hydrogen, acetylene, chlorine, were taken from commercial cylinders.

Since the refractivity of hydrogen is very much less than that of oxygen, and since it was feared that it might be contaminated with that, a second observation was made of the gas obtained by passing it through a solution of potassium pyrogallate, as recommended by Hempel, and then drying it.

Methane was supplied in a cylinder by the Lightfoot Refrigeration Co. Ltd., and the purity was stated to be 97·19% methane, CO_2-0·67% and nitrogen 2·14%. Necessary corrections were made for the impurities knowing their depolarisation factors. Also, for a second time, the gas was prepared by heating a mixture of very pure sodium acetate (1 part) and barium oxide (4 parts) and purifying it by passing through caustic soda and strong sulphuric acid. The values agree well.

Ethylene, propane, butane and isobutane, and methyl chloride of nearly 100% purity, helium of 96% and ethane about 90 were supplied by the Ohio Chemical Manufacturing Co. The Raman spectrum of ethane taken by Bhagavantam shows very small impurities of either butane or propane which, however, will not affect the result to any considerable extent, since they themselves have got low depolarisation factors.

Argon was supplied by the Lightfoot Refrigeration Co. Ltd., with a purity of 97%, the impurities being nitrogen 1·7% and oxygen 1·3%. No attempt, however, was made at further purification since it was feared that more impurities might be added in the course. The value as obtained was corrected for both the impurities.

In the case of low boiling liquids, which are gaseous or have high vapour pressure at the room temperature (28°C), it was found sufficient to evacuate the cross and other tubes up to the liquid and then slowly allow the liquid to evaporate into the cross. Kahlbaum's or Merck's purest chemicals only were used. Such chemicals were methylamine and ethylamine, formaldehyde and acetaldehyde, methyl ether and ethyl ether, acetone, allyl alcohol, methylene chloride, chloroform and carbon tetrachloride. Silicon tetrachloride also gave sufficient vapour for examination.

Only the purest chemicals were used in the following preparation of gases. Such methods were chosen as would give very pure gas unmixed with others.

Hydrogen sulphide.—This was obtained from good quality pyrites and H_2SO_4, the gas being subsequently passed through strong H_2SO_4.

Hydrochloric acid gas was prepared from sodium chloride and strong H_2SO_4. It was dried by passage through H_2SO_4 and P_2O_5.

Hydrobromic acid gas was easily obtained by dropping aqueous solution of the acid on to P_2O_5 in a flask and subsequently drying it over P_2O_5.

Hydriodic acid gas was obtained by dropping red phosphorus with water as vehicle, on to iodine and water contained in a flask. It was passed through red phosphorus and P_2O_5.

Nitric oxide.—Sulphuric acid dropped slowly over excess of potassium nitrite in water, produced the gas copiously. An alternative method of preparing the pure gas by the action of a strong solution of SO_2 on air-free dilute nitric acid was also tried. The gas was purified by passing it through tubes containing strong potash solution, solid potash, strong H_2SO_4 and P_2O_5. The values obtained for the gas prepared in the two ways agree well.

Carbon-monoxide.—Formic acid dropped in small quantities on to concentrated H_2SO_4 contained in a flask gave very pure CO.

Silicon tetrafluoride.—Thoroughly purified sand in excess mixed with sodium fluoride was heated in a flask to remove even the smallest trace of air or moisture. Strong H_2SO_4 was dropped through a funnel and the mixture was heated. The apparatus was thoroughly washed with the gas four times, and the gas examined was of the fifth filling. It was found that there was no cloud formation or decomposition. The scattered light was of the usual blue colour.

The gas was allowed to remain in the cross and again examined after 24 hours setting, when it gave identical values. No decomposition had set in even after a day.

Carbonyl sulphide.—Ammonium thiocyanate solution was dropped on to sulphuric acid (1 water to 4 of acid) in a flask, and the gas was passed through 20 c.c. of 33% sodium hydroxide to absorb 2·5% CO_2 evolved. It was dried by passage through strong H_2SO_4 and P_2O_5.

In all the above cases, the apparatus from the cross to the flask containing the chemicals for the production of the gas, was made leak-tight and completely exhausted before the evolution of the gas, thus securing the maximum purity for the gas.

5. *Results.*

In the following table are set forth the depolarisation factors (the ratio of intensity of the weak to the strong component) for the various molecules with their corresponding optical anisotropy calculated from Ramanathan's[8] formula. It will be seen that those of Ramkrishna Rao[9] are in good agreement with those of the author, in some cases within the limits of personal error. For argon, the depolarisation after correction for nitrogen and oxygen agrees with that of Cabannes and Granier; Rayleigh's value is much less. It would seem necessary to correct anew Rayleigh's value, since he assumed the depolarisation for nitrogen as 4·06%, whereas it is only 3·55%. The corrected value will give now 0·49%.

The value given by Lord Rayleigh for the depolarisation of light scattered transversely by helium was not anything definite, but he gave an upper limit as 6·5%. Owing to the low refractivity its scattering power is rather small and, therefore, observation is difficult. Here also only an upper limit is given, below which it was found impossible to go; but it has been considerably reduced to 3%.

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[8] Ind. Jour. Phps., 1, p. 420 (1927).

[9] Ind. Jour. Phys., 2, p. 61 (1927).

TABLE I

Substance.	Chemical Formula.	$r \times 10^2$	$\delta \times 10^3$ calculated.
Organic.			
Methane from cylinder and corrected	CH_4	1·14	9·6
Pure gas	...	1·12	...
Ethane	C_2H_6	1·30	11·0
Propane	C_3H_8	1·51	12·8
Butane	C_4H_{10}	1·51	12·8
Isobutane	C_4H_{10}	1·03	8·7
Ethylene	C_2H_4	2·92	25·2
Acetylene	C_2H_2	4·52	39·8
Methyl chloride	CH_3Cl	2·04	17·4
Methylene chloride	CH_2Cl_2	2·93	25·3
*Chloroform	$CHCl_3$	1·78	15·1
Carbon tetrachloride	CCl_4	0·62	5·2
Methylamine	CH_3NH_2	0·77	6·5
Ethylamine	$C_2H_5NH_2$	0·97	8·2
Formaldehyde	$H{\cdot}CHO$	1·88	16·0
Acetaldehyde	$CH_3{\cdot}CHO$	2·68	23·1
Methyl ether	$CH_3\text{-}O\text{-}CH_3$	1·56	13·2
Ethyl ether	$C_2H_5\text{-}O\text{-}C_2H_5$	2·51	21·6
Acetone	$CH_3{\cdot}CO{\cdot}CH_3$	1·62	13·7
Allyl alcohol	$CH_2{:}CH{\cdot}CH_2$ OH	2·40	20·6

TABLE I—*continued.*

Substance.	Chemical Formula.	$r \times 10^3$	$\delta \times 10^3$ calculated.
Inorganic gases.			
Air	...	4·15	36·3
Oxygen	O_2	6·50	58·6
Nitrogen	N_2	3·55	30·9
Hydrogen (from cylinder and corrected)	H_2	2·71	...
Pure gas	...	2·57	22·2
Chlorine	Cl_2	4·07	35·6
Carbon dioxide	CO_2	9·72	91·2
Nitrous oxide	N_2O	12·47	122·0
Hydrchloric acid gas	HCl	0·71	6·0
* Hydrobromic acid gas	HBr	0·84	7·1
* Hydriodic acid gas	HI	1·27	10·7
Nitric oxide (gas by both methods)	NO	2·68	23·1
Carbon monoxide	CO	1·30	11·0
Ammonia	NH_3	0·98	8·3
Hydrogen sulphide	H_2S	0·93	7·8
* Sulphur dioxide	SO_2	3·11	26·9
* Carbonyl sulphide	COS	8·77	81·4
Silicon tetrachloride	$SiCl_4$	1·64	13·9
Silicon tetrafluoride	SiF_4	3·11	26·9
Argon (uncorrected value)	A	0·71	...
(Corrected value)	...	0·56	4·7
Helium	He	<3·0	...

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* Filters, either quinine sulphate or black paper to cut off completely the incident beam when observation was not made, or both, were used in all these cases.

6. *Anisotropy of Gaseous Molecules.*

From a treatment of the scattering of light on the electromagnetic theory, Ramanathan [10] derived

$$r = \frac{6\delta}{\frac{5RT\beta n}{N}\left(\frac{\mu^2+2}{3}\right)^2 + 7\delta}.$$

where r is the depolarisation of the scattered light
R the gas constant
T the absolute temperature
β the compressibility
n the number of molecules per c.c.
N ...... gram molecule, and
μ the refractive index
for a molecule in a fluid state. The anisotropy δ contains only A, B, C, the optical moments induced in the molecule in a field of unit intensity along its 3 principal axes respectively and is given by

$$\delta = \frac{A^2+B^2+C^2-AB-BC-CA}{(A+B+C)^2}$$

so that for an isotropic molecule or atom for which $A=B=C$, $\delta=0$ and consequently r vanishes. In other words, the light scattered transversely by such molecules and atoms is completely polarised.

The above formula was later on modified by Ramanathan [11] from considerations of the fluctuations of dielectric constant in the fluid state to

$$r = \frac{6\delta}{\frac{5RT\beta n}{N} + 7\delta}$$

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[10] Proc. Ind. Assn. Cult. Sci., Vol. VIII, pp 1-22 and 181 (1923).
[11] Ind. Jour. Phys., 1, p. 420 (1927).

In all the above cases studied, the temperature was 28° C and far above the boiling points of most of the compounds, the pressure being one atmosphere or less. For a gas, sufficiently rare to obey Boyle's law, the above formula can be reduced to a first approximation to

$$\frac{6\delta}{5+7\delta}$$

since for the above conditions

$$\frac{RT\beta n}{N}=1$$

The anisotropy factors given in the above table are calculated using this formula. The correction, however, is very small.

7. *Discussion.*

While in the main, supporting Ramakrishna Rao's conclusions, some new light is thrown on the effect of different radicals. Polar groups seem to affect the values greatly. Very interesting results are also got from a study of the symmetrical tetrahedral molecules.

1. In the series, methane, ethane, propane and butane, the optical anisotropy increases from the lowest member up to propane even though differing by little, and then remains the same for the next member also. In comparison to the length of the chain, the anisotropy is small. This suggests that the length of the chain, perhaps, does not count after a certain stage. From vapours done by I. R. Rao, it is evident that even for octane, the depolarisation is only 1·66%. The four valencies of the carbon being distributed in space, the molecule more or less assumes a nearly isotropic structure.

2. Substitution of $-CH_2$ in the middle of the hydrocarbon instead of at the ends decreases the anisotropy. Propane and butane have the same depolarisation, *viz.*, 1·51, while isobutane which has got a more symmetrical structure has

only 1·03. Rao's work on vapours also clearly shows this markedly. The following figures are taken from his paper.

TABLE II

Substance.	$r \times 10^3$	$\delta \times 10^3$	Substance.	$r \times 10^3$	$\delta \times 10^3$
Propyl alcohol	1·19	10·5	Propyl bromide	2·03	17·3
Butyl ,,	1·62	13·8	Butyl ,,	...	...
Isobutyl ,,	0·77	6·9	Isobutyl ,,	1·53	13·0
Amyl ,,	1·20	10·1			
Isoamyl ,,	1·03	8·3			

It is assumed in all these cases, therefore, that the molecules become more and more isotropic due to substitution in the middle, whether it be $-CH_2$, Br or $-OH$ as exemplified in the above cases.

3. With increasing unsaturation, the optical anisotropy increases. Ethane, ethylene and acetylene afford an interesting series as an example. This is what is to be expected from Ramanathan's theory.[12]

In all the above three compounds, it is chiefly the distance between the two carbon atoms that counts, for with the increasing strength of binding, the distance between the atoms must presumably diminish. The distance C—C between carbons in ethane may be taken to be the same as in diamond which is known from X-ray analysis to be 1·54 A.U. The distance C=C in ethylene may be safely assumed to be less than the value 1·42 A.U., which is the distance between the carbon atoms in graphite. 1·35 A. U. is probably a good estimate. Hedfeld and Mecke[13] have recently examined the band spectrum of acetylene and from the rotational structure, they arrived at 1·19 A. U. for the distance $C \equiv C$ between the carbon atoms in this gas. In his theory, Ramanathan arrives at the depolarisation factor as a function of *d* through the mutual influence of the induced doublets in the atoms, and it can be easily seen from his argument that when *r* increases, the distance *d* between the atoms decreases.

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[12] Proc. Roy. Soc., A, 107, 684 (1925).

[13] Zeit. f. Phys., 64, p. 151 (1930).

Now arranging the three cases in order with depolarisation and interatomic distances between the carbon atoms, one finds general agreement with his theory.

TABLE III

Substance.	Formula.	$r \times 10^2$	d in A.U.
Ethane	H_3C-CH_3	1·30	1·54
Ethylene	$H_2C=CH_2$	2·92	1·35
Acetylene	$HC\equiv CH$	4·52	1·19

Even the presence of a double bond in the molecule enhances the optical anisotropy, as evidenced in formaldehyde acetaldehyde, acetone and allyl alcohol.

4. The effect of gradual substitution of chlorine in methane is very interesting to note. The optical anisotropy increases up to methylene chloride and then comes down to even below the methyl chloride value for chloroform. It is interesting, however, to note that the direction of electric moment is different in the two cases, with respect to the axis of maximum polarisability, in methyl chloride being coincident while in chloroform they are at very nearly right angles. Whether this fact has anything to do with the lowering of the optical anisotropy, we shall have occasion later on to refer. For carbon tetrachloride again, the depolarisation factor reaches the minimum. This is very easily accounted for on the supposition that the molecule of CCl_4 is very nearly tetrahedral in form and therefore nearly isotropic optically.

5. With a highly refractive oxygen, the case of methyl ether presents an anomaly; its anisotropy is comparable to that of propane when it should have been much greater than that of the corresponding hydrocarbon. Ether is polar but has a negative Kerr constant. Elsewhere, in this section it is shown how low anisotropy and negative Kerr constant values for polar molecules go together. As examples, we can cite the cases of sulphur-dioxide, chloroform, amines and alcohols. It is perhaps due to this fact that the anisotropy of methyl ether is not greater.

6. An interesting departure is noted in methylamine and ethylamine. The optical anisotropy is considerably lower than that for the corresponding hydrocarbons. So far, we have met with cases where, either due to substitution or introduction of double bond the anisotropy increases. But, here there is a definite departure from the general effect of substitution.

On looking into Rao's tables, it is found that in the alcohol series also, with the exception of methyl alcohol, the anisotropy of the alcohol is much less than that for the corresponding hydrocarbon. The following figures for alcohols taken from Rao's paper clearly show it.

TABLE IV

Hydrocarbon.	$r \times 10^2$	$\delta \times 10^3$	Corresponding alcohol,	$r \times 10^2$	$\delta \times 10^3$
Methane	1·14	9·6	Methyl alcohol	1·64	14·3
Ethane	1·30	11·0	Ethyl ,,	0·88	7·7
Propane	1·51	12·8	Propyl ,,	1·19	10·5
Isobutane	1·03	8·7	Isobutyl ,,	0·77	6·9
Pentane	1·28	11·5	Amyl ,,	1·20	10·1

It is well-known that polar molecules possessing in general an OH or NH_2 group have negative or very small positive Kerr constants. In all such cases, the direction of the permanent electric moment is found to be at right angles or nearly so to the axis of maximum polarisability. The converse of the above, namely, these two being at right angles does not necessarily indicate negative Kerr constant values for the molecules. This fact shows clearly that OH and NH_2 groups which are responsible for the negative Kerr constants are also responsible for decreasing the optical anisotropy of the molecules. That the permanent moment directed at whatever angle to the axis of maximum polarisability affects the anisotropy has been made clear from experiments on light-scattering on various dipole gases. Strangely enough, negative Kerr constant values and low anisotropy seem to go together. But how the two mutually affect is at present difficult to understand.

Hence the polar groups either enhance or lower the anisotropy with respect to the hydrocarbon depending on the nature of the group introduced, whether negative or positive.

7. Considering the inorganic compounds, one interesting fact emerges out, namely, that while homopolar compounds like O_2, N_2, H_2 and Cl_2 and non-polar molecules such as CO_2 and N_2O have large depolarisation, polar compounds of the type HCl, H_2S, NH_3 show only very small depolarisation, giving only the anisotropy of the ions. The bindings in the two types are quite different.

8. HCl, HBr and HI show increasing depolarisation in that order. This is not surprising in view of the fact of greater refractivity of the Br than Cl, and of I than Br. The respective ions therefore possess increasing anisotropy.

9. NO and CO though very slightly polar show surprisingly small depolarisation, especially the latter. This might be due to unused valencies.

In the case of CO_2 we can imagine the two nuclei to be very close and then the two electrons of the carbon to move round both the nuclei; in which case less anisotropy will result.

A similar explanation for NO also will account for the low depolarisation.

10. COS comes midway between CO_2 and CS_2 in its properties. But Zahn and Miles[14] have shown recently the presence of permanent electric moment of $0{\cdot}65 \times 10^{-18}$ C. G. S., electrostatic units, in COS. The lower depolarisation of 8·77 for COS, lower than either CO_2 or CS_2 points also to the polar nature of the molecule (Rao gives 11·1 for depolarisation of CS_2).

11. Silicon tetrafluoride and silicon tetrachloride also show incomplete polarisation even though to different extents, the former to 3·11% and the latter to 1·64%. The former value is surprisingly large for a tetrahedral molecule. Even the plausible explanation of the isotopes of chlorine giving rise to anisotropy does not seem to hold good. Hydrogen or fluorine is not known to have isotopes, but CH_4 and SiF_4 are anisotropic. Moreover isotopes are likely to influence only the infra-red absorption or the Raman lines[15] but not the classical scattering. It has been so far an unexplained fact, as to why even tetrahedral molecules like CH_4 and CCl_4 should show any optical anisotropy at all. It was usual to explain it by assuming a slight departure from the tetrahedral model for the molecule or by assuming the two pairs of electrons from the two L_1 and L_2 levels to be different, thereby giving anisotropy to the carbon atom itself. But recently, Pauling[16] from the quantization of the bond eigen-functions concludes that the four bonds are equivalent and directed toward tetrahedron corners.

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[14] Phys. Rev., 32, p. 497 (1928).

[15] Langseth. Zeit. fur. Physik, 72, p. 350 (1931).

[16] Jour. Amer. Chem. Society, 53, p. 1367 (1931).

It was, therefore, surprising why isotropic molecules should ever show depolarisation instead of complete polarisation in the transverse direction.

The primary question before the above can be answered is why even CCl_4 and CH_4 should show such widely differing values, the latter having double the value of the former? On the other hand, one would expect CCl_4 to show greater depolarisation on account of the larger refractivity of the chlorine atoms, even supposing for the present that the structure of the molecules possesses a slight departure from perfect tetrahedral symmetry, though there is no support for esuch an argument.

If consideration is given to the relative sizes of the central atom to the surrounding ones, the matter is exceedingly easy to comprehend. On the view that anisotropy increases if the central atom, which is supposed to be the same for a number of molecules, is surrounded by less and less heavy atoms the above observations on CH_4, CCl_4, SiF_4 and $SiCl_4$ can be explained without assuming any departure from symmetry for the molecule. The converse also holds good, the anisotropy increasing where four similar atoms have a central heavier atom successively.

TABLE V.

Compound.	$r \times 10^2$	Compound.	$r \times 10^2$	Compound.	$r \times 10^2$
CCl_4	0·62	$SiCl_4$	1·64	CCl_4	0·62
CH_4	1·14	SiF_4	3·11	$SiCl_4$	1·64

$TiCl_4$ and $SnCl_4$ must therefore be more and more anisotropic while the anisotropy for SiH_4 will perhaps exceed any so far found for a molecule of RX_4 type. Also the anisotropy for CBr_4 vapour must be the lowest ever found, smaller than even those for the rare gases or CCl_4.

The above clearly indicates that for anisotropy in molecules, mere geometry of form is not sufficient to account for it.

12. Argon has been found to be anisotropic also. For ordinary molecules, anisotropy is genuine; for rare-gas-like ions, the anisotropy may be caused by the deformation produced by the surrounding ions; for isotropic molecules, the explanation lies in the relative sizes of the constituent atoms; but for rare gases, it is quite incomprehensible why there should be any anisotropy at all. Till more experiments are conducted on it, we will avoid all speculation for the present.

Further work as to the nature of the imperfect polarisation of the transversely scattered light in argon is in progress and will, it is hoped, enable us to decide whether argon possesses any real anisotropy or not.

The author is indebted to Prof. Sir C. V. Raman for his very keen interest, guidance and suggestions in the above work.

14

Modern Differential Geometries

By

D. D. KOSA[illegible]BI

In considering the relationship between various spaces recently constructed as generalizations of Riemann spaces, I have come to certain conclusions published elsewhere in detail, of which this is a brief survey. Roughly, the work seems to bear the same relation to the usual differential geometries, affine or otherwise, as does that of Frl. Emmy Noether and Berwald, to the Riemannian geometry; the investigations of Douglas are probably a special case. In the following, the tensor summation convention is used, and differentiation to x^h and $\dot{x}^k$ is respectively denoted by a comma and a semicolon with the corresponding subscript to follow.

A K-space is defined by the integral curves of

$$(1) \qquad \ddot{x}^i + \bar{a}^i(x, \dot{x}, t) = 0 \qquad i = 1 \ldots n$$

which are assumed to be such that for some part of the (x, t) domain, there is one and only one regular solution, for a given set of values $\dot{x}$. When one tries to deduce these equations from a variational principle

$$(2) \qquad \delta \int f(x, \dot{x}, t) dt = 0$$

one is at once led to the following equations for the integrand f, the metric of the K-space:

$$(3) \qquad \frac{\partial^2 f}{\partial \dot{x}^i \partial \dot{x}^j} - \dot{x}^i \frac{\partial^2 f}{\partial x^i \partial \dot{x}^j} - \frac{\partial^2 f}{\partial \dot{x}^j \partial t} + \frac{\partial f}{\partial x^j} =$$

with the subsidiary condition for non-triviality,

$$(3a)\quad \Delta:\quad \frac{\partial^2 f}{\partial \dot{x}^i\,\partial \dot{x}^j}\neq 0$$

There is not, in general, a non-trivial solution for the most general set of a^i. But if, one postulates that any at least twice differentiable function $\psi\,(f)$ be also a possible metric with f, one is led on substitution to

$$(4)\quad \frac{\partial f}{\partial t}\equiv -a^i\frac{\partial f}{\partial \dot{x}^i}+\dot{x}^i\frac{\partial f}{\partial x^i}+\frac{\partial f}{\partial t}=0$$

This corresponds to a conservation principle, and means precisely that the integrand f must be a constant along the “paths,’ ’defined by (1). Differentiating (4) successively to $\dot{x}^k$. and substituting in (1) leads to a first order system for f:

$$(5)\quad \frac{\partial a^i}{\partial \dot{x}^k}\quad\frac{\partial f}{\partial \dot{x}^i}-2\,\frac{\partial f}{\partial x^i}=0$$

The first compatibility condition for (4) & (5) is seen to be

$$(6)\quad \epsilon^i\,\frac{\partial f}{\partial \dot{x}^i}-\frac{\partial f}{\partial t}=0\qquad\qquad \epsilon^i=a^i-\frac{1}{2}\dot{x}^k\frac{\partial a^i}{\partial \dot{x}^k}$$

This makes it clear that the spaces for which the a^i are homogeneous of degree two in $\dot{x}$ are simpler than the rest, inasmuch as (4) and (1) are consequences of (5), provided f does not contain t explicitly.

The differential invariants of the space are to be had from the usual conditions of compatibility. The partial derivatives $\frac{\partial f}{\partial x^i}$ being eliminated by means of (5) whenever possible, we have

$$(4)\,(5)\quad P^i_j\,\frac{\partial f}{\partial \dot{x}^i}=0$$

$$(5)\ (5)\quad R^{i}_{\ jk}\frac{\partial f}{\partial \dot{x}^{i}}=0$$

where

$$(7)\quad P^{i}_{\ j}=a^{r}a^{i}{}_{;r,j}-\dot{x}^{r}a^{i}{}_{,r;j}-\frac{1}{2}a^{i}{}_{;k}a^{k}{}_{;j}-\frac{\partial}{\partial t}a^{i}{}_{.j}+2a^{i}{}_{j}$$

$$R^{i}_{\ jk}=\frac{2}{3}\left[\frac{\partial}{\partial \dot{x}^{j}}P^{i}_{\ k}-\frac{\partial}{\partial \dot{x}^{k}}P^{i}_{\ j}\right]$$

These are the generalized Riemannian curvature tensors for the K-space.

As a special case, for instance, we find that with the usual co-efficients of affine connection, a term of the form

$$^{(n)}A_{i_1\,i_2\ldots\ldots}\dot{x}^{i_1}\,\dot{x}^{i_2}\ldots\ldots\dot{x}^{i_n}$$

enters into an invariant f, if and only if $^{(n)}A_{i_1\ldots i_n}$ is a tensor with vanishing covariant derivative. This settles the problem of the expansion of f as a polynomial in $\dot{x}$. Further, we have the Hamilton's principle directly from (3):

$$(8)\quad \frac{d}{dt}\left(\dot{x}^{i}\frac{\partial f}{\partial \dot{x}^{i}}-f\right)+\frac{\partial f}{\partial t}=0$$

So that, for an f not containing t explicitly, but homogeneous of any order except the first in $\dot{x}$, or even obeying

$$\dot{x}^{i}\frac{\partial f}{\partial \dot{x}^{i}}-f=\phi(f)\not\equiv 0$$

we have the property $\frac{'df}{dt}=0$ also.

A parallelism, or, to be accurate, two such, can be derived on the assumption that there exists a derivate $D(u)$ which is a vector with u, such that (1) are obtained directly from $D(\dot{x})=0$. Even under a general law of vector transformation

$$\bar{u}^i = F^i_j\, u^j \qquad (\bar{x} \longleftrightarrow x) \quad [F^i_j] \neq 0$$

the conditions above lead at once to

$$(9) \quad D(u)^i \equiv \ddot{u}^i + \gamma^i_k u^k + \epsilon^i \qquad \epsilon^i = \alpha^i - \gamma^i_k \dot{x}^k$$

Moreover, ϵ^i is also a vector, and the law of transformation of the γ^i_k is given by

$$(10) \quad \bar{\gamma}^i_k\, F^k_j + \frac{d}{dt}\, F^i_j = F^i_k \gamma^k_j$$

There is a "restricted" derivate, obtained by leaving off the vector ϵ^i.

$$(11) \quad \mathscr{D}(u)^i \equiv \ddot{u}^i + \gamma^i_k u^k$$

This is also a contravariant vector with u. It can further be defined for covariant vectors as well, and will be a covariant vector itself, with the proper law of transformation for γ^i_k.

$$\mathscr{D}(u)_i = \ddot{u}_i + \gamma^i_j u^j \qquad \bar{u}_j = \phi^i_j u_i \text{ etc.}$$

The process obviously gives a derivate for tensors of any rank, as in the usual case. Parallelism would be defined as the vanishing of the derivate, along the particular curve in question.

The determination of the γ^i_k requires further assumption, of which the simplest is that the equations of variation of (1) can be written as

$$12) \qquad \ddot{u}^i + u^k \frac{\partial \alpha^i}{\partial \dot{x}^k} + u^r \frac{\partial \alpha^i}{\partial x^r} \equiv \begin{cases} D^2(u)^i + \phi^i(x, \dot{x}, t) \\ \mathscr{D}^2(u)^i + \psi^i(x, \dot{x}, t) \end{cases}$$

This gives, on the assumption that u is parallel displaced along the base, either in the general or the restricted sense,

$$\gamma_k^{\,i} = \frac{-}{2} \qquad \partial \ddot{a}^{i}$$

It is found as a trivial consequence that a covariant derivative independent of the direction exists only in spaces with symmetric affine connections, under the assumptions of this paper. Furthermore, laws of vector transformation that involve the vector in the co-efficients F^i_j are in general not feasible.

There remain certain obvious consequences of the theories to be noted. First, the laws of vector transformation can be assimilated to those of a group of matrices. Again, as the formula (10) shows, all the γ^i_k can be made to vanish if there exists a transformation for which the co-efficients are equal to a family of vectors, which is *biparallel* along the base, *i. e.*, whose restricted derivates all vanish along the given curve. The transformation then allows a reduction of the equations of variation (12) to the normal form

$$\text{(13)} \qquad \ddot{u}^i = -\frac{1}{2} P^i_j \, u^j$$

This is particularly useful for the discussion of conjugate foci, and problems of stability. Now the said transformation can always be shown to exist, for the ordinary laws of vector transformation in an infinity of ways. Stability thus comes to the investigation of the roots of the equation

$$\text{(14)} \qquad \delta^i_j \, \lambda + \frac{1}{2} P^i_j \qquad = 0$$

which must all be real and negative for complete stability. Furthermore, P^i_j being a mixed tensor, these roots are known to be invariants of any non-singular point transformation.

In closing, I point out that affine relativity theories of the unified gravitational and electromagnetic fields can be constructed, to include the work done recently by Paolo Straneo, Einstein and Meyer, by means of assuming a restricted derivate, with the corresponding "bipaths" as derivable from a metric, while the vector that represents the residual co-efficients is capable of being interpreted as one related to the electromagnetic forces. The foregoing immediately gives the curvatures of the affine space.

ALIGARH MUSLIM UNIVERSITY,
March 8, 1932.

15

On Discontinuous Fluid Motion Under Different Thermal Conditions.

By

Sudhansu Kumar Banerji and Vishnu madhav Ghatage.

(Plates XI to XX)

CONTENTS.

1. Introduction.
2. Experimental methods of introducing temperature and velocity discontinuities in a fluid initially stationary or moving.

Part. I. Thermal discontinuity in a liquid initially at rest.

3. Experimental arrangement for introducing a thermal discontinuity in still water (*a*) by means of a plane shutter in a rectangular tank, and (*b*) by means of a thin hollow cylinder.
4. General discussion of the phenomena observed after a thermal discontinuity is introduced in still water.
5. Effect of initial conditions, boundaries, etc., on subsequent development of vortices.

Part. II. Thermal discontinuity in a moving liquid.

6. Experimental arrangement for introducing a thermal discontinuity in moving liquids.
7. General discussion of the phenomena observed at the surface of discontinuity between cold and warm currents.

8. The growth of vortices at the surface of discontinuity.
9. The slope of the surface of discontinuity.
10. The change in the surface row of vortices and its direction with time.
11. Paths of particles at the surface of discontinuity.
12. Summary.

1. *Introduction.*

The present investigation was undertaken with the object of making a detailed study of the phenomena occurring at the discontinuous boundaries between portions of liquids under different thermal conditions. The instability of the "liquid surface" which separates the portions of a liquid, which are at the same temperature but moving with different velocities, has formed the subject of a large number of investigations.[1] It is known that the surface of discontinuity between two portions of a fluid, owing to fluctuations in the flow, assume at first a wavy form and that the waves advance with a velocity which is equal to the mean of the velocities of the two portions. If the motion be assumed to be steady then Bernoulli's theorem indicates that when the surface of discontinuity has assumed a wave pattern, there is an excess of pressure at the crests of each portion of the fluid and a defect of pressure at the troughs. But since, the crest in one portion of the fluid is the trough in the other portion, this distribution of pressure cannot possibly remain steady. The fluid in the region of excess pressure will tend to move towards the neighbouring region of reduced pressure with the result that the undulation of the surface of discontinuity will become more and more marked. Finally the surface will break down into a large number of eddies.

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[1] An elementary discussion of this case is to be found on pp. 225-226 of "The Physics of Solids and Fluids" by Ewald, Pöschl and Prandtl (1930).

In his memoir [2] on "the Dynamics of the Circular vortex with applications to the atmosphere and atmospheric vortex and wave motions," Prof. V. Bjerknes has explained how the "surface of discontinuity" develops into cyclones and anti-cyclones in the atmosphere. His diagram on p. 23 which has been reproduced as fig. 1 in this paper shows clearly how a "surface of discontinuity" in the initial stage when it has developed into a wave pattern consists of elemental vortices.

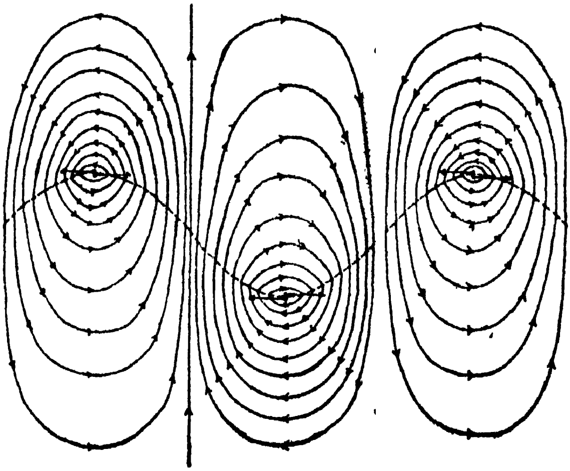

Fig. 1

A rigorous mathematical discussion of the formation of vortices from a surface of discontinuity between two fluids, moving one above the other with equal velocities but in opposite directions, has recently been given by Rosenhead.[3] Assuming $y=a \cos kx$ to be the initial form of the surface of discontinuity, he shows that this surface, instead of growing according to Rayleigh's formula [4]

$$y=ae^{kUt} \cos kx,$$

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[2] Geofysiske Publikationer, Vol. II, No. 4 (1921).

[3] Rosenhead, Proc. Roy. Soc., Vol. 134, A, pp. 170-192 (1931). A correction to the formula originally given in this paper has been published in Proc. Camb. Phil. Soc., Vol. 28, p. 44, (1932). The formula here given is the corrected formula.

[4] Scientific Papers, Vol. I, pp. 474-487.

grows according to the law

$$y = ae^{kUt}\cos kx + \tfrac{1}{2}\,Uk^2a^2\left(te^{2kUt} - \frac{1}{2kU}\sinh 2kUt \right)\sin 2kx,$$

correct to the second order of small quantities. In this formula a is the initial amplitude, $2\pi/k$ the dominant wave length, U the velocity of the upper stream, and $-$U the velocity of the lower stream. The amplitude of the disturbance represented by the second term grows much more rapidly than that of the first and ultimately dominates it. The second term is anti-symmetrical with respect to the crest of the original wave and its effect is, therefore, to give the original cosine curve a shape somewhat like that of a breaker in the first stages of its growth, instead of the symmetrical shape suggested by the Rayleigh solution. In determining the ultimate shape of the surface, Rosenhead adopts an approximate numerical method. Instead of assuming a continuous distribution of vorticity over the surface, he approximates to it by a distribution of finite "elemental" vortices and then follows up the paths of these vortices by a numerical step by step method. On p. 187 of the Royal Society paper, he has given a figure indicating the form of the surface (replaced by 12 elemental vortices per wave length) at various stages of the motion. This figure, owing to its theoretical importance, has been reproduced as fig. 2 in this paper. It is seen that the effect of instability upon a surface of discontinuity of sine form is to produce concentrations of vorticity at equal intervals along the surface and it is also seen that the surface of discontinuity tends to roll up round these points of concentration with an accompanying increase in the amplitude of the displacement. Rosenhead in his second paper has pointed out that his theoretical analysis does not determine what wave length becomes ultimately dominant in the general disturbance.

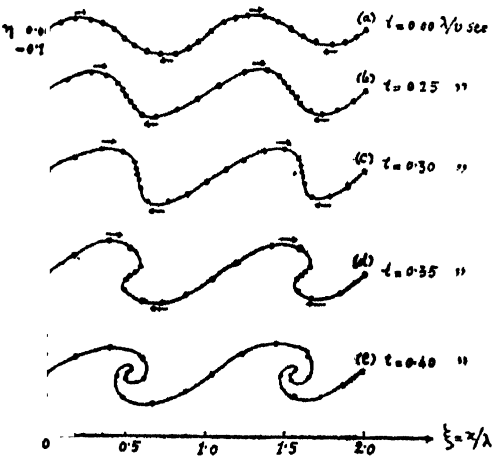

Fig. 2 (Rosenhead)

Rosenhead's analysis explains the phenomena when there is a simple discontinuity in motion only. But the discontinuity may be one of density or of both motion and density and in such cases the phenomena will be somewhat more complicated. A discontinuity in density of a simple kind may be introduced by making a cylindrical or a rectangular column of water in a large tank to have different temperature from the adjoining liquid, while a discontinuity in motion as well as density may be introduced by making two streams of water under different thermal conditions meet each other at various angles. In both cases the surface of discontinuity resolves itself into interesting patterns of three-dimensional moving vortices. The mode of production of vortices of this kind, their mechanism, the relationship of their dimensions, vorticity, etc., with the temperature difference at the surface of discontinuity and its slope, the depth of liquid, as well as the velocities of the incident currents and other factors have been discussed in the following pages.

The essential features of the motion are indicated below:—

(1) The surface of discontinuity at first assumes a wave pattern.

(2) The instability makes each crest or a trough to take up the form of a breaker and then roll round itself. A succession of spiral-shaped vortices is thus produced.

(3) In the direction of the motion, the vortices show in general a progressive increase in the number of convolutions.

(4) The successive vortices also show a progressive increase in amplitude (diameter).

(5) The greater the difference of temperature at the surface of discontinuity, the smaller is the diameter of the vortices. If there are no disturbing factors, then in the case of a very small difference in temperature, the vortices have enormous diameters.

(6) The vortices develop more rapidly the greater the difference of temperature at the surface of discontinuity.

(7) When a warm and a cold current meet each other, the slope of the surface of discontinuity, over and above the temperature difference, determines the dimensions of the vortices. The more inclined is the surface of discontinuity to the horizontal, the smaller is the diameter of the vortices.

(8) With the advance of time, the surface of discontinuity between cold and warm currents tends to become more and more horizontal and consequently the diameters of the vortices become larger and larger.

(9) The angle between the mean direction of cold and warm currents and the direction of the surface row of vortices becomes smaller if the initial difference of temperatures between the two currents is increased.

(10) As a rule the crests (within warm water) show greater development than the troughs (within cold water). The former always grow into well-defined vortices, but the latter merely assume the shape of breakers and seldom become full grown vortices. Considering both crest and trough vortices, the system is equivalent to double row of vortices.

(11) The vortices formed on surfaces of discontinuity of the type mentioned above are not exactly of the type known as Kármán street of vortices,[5] nor do they exactly obey the Kármán law. The ratio of the amplitude to wave-length does not, however, materially differ on the average from the Kármán value and this undoubtedly accounts for their stability.

The phenomena discussed in the present paper have wide application in nature. In the atmosphere, air masses at different temperatures frequently meet each other. A study of these atmospheric phenomena has led the Norwegian School of meteorologists and others to develop the interesting theory of the Polar Front. The life cycle of the extra-tropical cyclones as depicted by these authors bears a close analogy to the small scale phenomena observed at a surface of discontinuity produced under laboratory conditions. At the mouths of rivers where pure river water meets the sea water we have a density discontinuity, which is essentially the same as a temperature discontinuity. The eddies which develop at such surfaces of discontinuities are well known, but the precise relationships between their growths and their characters with the various factors which lead to their formation have not received adequate investigation.

2. *Experimental methods of introducing temperature and velocity discontinuities in a fluid initially stationary or moving.*

There are various ways in which a discontinuity of temperature, or of velocity or of both velocity and temperature may be introduced in a fluid. Two cases naturally come up for consideration, namely, (1) the case in which the fluid has been initially at rest, and a temperature discontinuity has been introduced in some part of it, and (2) the case in which the fluid has been initially in motion and a temperature discontinuity or both temperature and velocity discontinuities have been introduced in it.

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[5] Kármán and Rubach, Physical Zeitschr., Vol. 13, p. 49 (1912).

The introduction of a simple temperature discontinuity[6] in a fluid at rest appears to be more difficult than in a fluid in motion. The simplest case which is amenable to theoretical treatment is a cylindrical or rectangular column of water at different temperature from the rest of the liquid in a tank, both being initially at rest. But unfortunately a cylindrical or a rectangular column cannot be made to have different temperatures from the rest of the liquid without invoking the aid of some partitions. However thin these partitions may be, and however carefully they are removed, after the two portions of the liquid have assumed different temperatures, some slight disturbance is bound to be introduced in the process of removal tending to increase the instability of the surface of discontinuity.

Temperature discontinuities can, however, be introduced with comparative ease in a liquid in motion. The simplest method is to make two streams at different temperatures and flowing in different channels meet each other. Except the provision of suitable channels, this method does not require the use of a partition at the surface of discontinuity either initially or at a later stage of the motion. Details of the arrangement adopted for introducing temperature discontinuities in a liquid initially at rest or in motion will be presently described, but it is important to bear in mind that temperature discontinuities are closely similar to density discontinuities. Instead of using water at different temperatures, we can use brine and water, and indeed some previous investigators[7] have adopted this method for the investigation of the stability of superposed streams of fluids of different densities. The diffusion of temperature is, however, not the same as the diffusion of density, especially when the two liquids differ in chemical composition. The viscosity relationship of warm and cold water is also not the same as that of salt water and fresh water. Although therefore a temperature discontinuity is essentially the same as a density discontinuity dynamically, yet they are not exactly identical. In nature, particularly in the atmosphere, temperature discontinuity is more common than density discontinuity. Where fresh river water pours out into the sea more or less at the same temperature, we have undoubtedly a density discontinuity, but in the "gulf-stream" we have a temperature discontinuity. As in the atmosphere, so in the ocean when two currents of different origin meet each other, we come across not infrequently with a typical surface of temperature discontinuity.

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[6] The convection currents in liquids caused by heat sources, such as a heated circular disc placed at the bottom of a tank, or a heated side of a tank, or heated electric coils or wires at different points of the tank, have been studied in some detail by Terada and Hattori, Report of the Aeronautical Research Institute, Vol. II, No. 2 (1926), Vol. III, No. 1 (1928), Vol. IV, No. 12 (1929). These are cases in which warm water forces its way through cold water in a complex manner. They do not represent cases in which warm and cold water had been initially in juxtaposition with each other along a simple geometrical surface, the latter undergoing progressive development, such as those studied in this paper.

PART I.

Thermal discontinuity in a liquid initially at rest.

3. *Experimental arrangement for introducing a thermal discontinuity in still water* (*a*) *by means of a plane shutter in a rectangular tank, and* (*b*) *by means of a thin hollow cylinder.*

A plane removable shutter P working along vertical guides fixed in the sides of a rectangular glass tank divides the water into two parts [fig. 3 (*a*)]. A sheet of rubber is fixed at the bottom of the tank to prevent intermixing and to have a cushion effect when the shutter rests in water. A thermal discontinuity is introduced by either lowering or raising the temperature of water on one side of the shutter by means of an electric coil, or by ice, or hot water. The shutter is removed vertically upwards with the help of a ball-bearing pulley and clockwork, which ensures a uniform speed.

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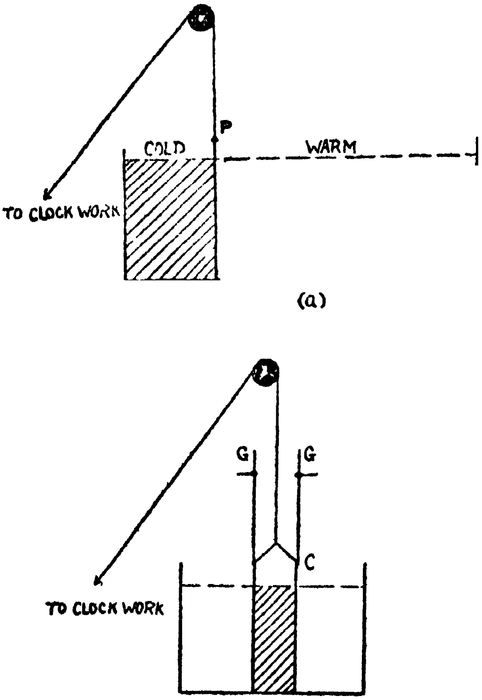
[7] G. I. Taylor, Proc. Camb. Phil. Soc., Vol. 23, p. 730 (1927) ; Q. J. R. Met. Soc., Vol. 53, p. 201 (1927). For an interesting theoretical treatment of this problem, see Goldstein, Proc. Roy. Soc., Vol. 132 A, p. 524 (1931).



(a)

(b)

Fig. 3

In order to make the phenomena occurring at the surface where the two columns of water meet, when the shutter is removed, visible, one of the columns is coloured by fuchsine or alizarine. Alizarine (made into a paste with ammonia) is better than fuchsine for mass colouring owing to the fact that it diffuses more slowly in water. This method gives the general relative movement of the two columns but fails to give the details of the motion at any point or of an individual particle. Nor can we visualise in this way the stream lines in the motion. To trace the form of the surface of discontinuity, a fine vertical line of red ink is drawn on the surface of the shutter before its insertion in the tank. When the shutter is inserted, the adjoining water gets coloured along the line and when it is removed, the coloured line remains hanging in the water. The subsequent growth of the surface of discontinuity is shown in a conspicuous manner by the distortions of this coloured line.

For photographic purposes the rear of the tank is covered with thin white paper and is illuminated by means of two 500 Watt Phillips lamps or by sunlight. The surface of discontinuity as depicted by the coloured line is then photographed at various stages of its growth by instantaneous exposures (1/25th second).

The simplest surface of discontinuity is undoubtedly obtained when we have superposed streams of fluid of different densities moving with unequal velocities in the same direction, or with equal or unequal velocities in opposite directions. In this case the form of the surface of discontinuity is not affected by gravity. But in nature we seldom get a case where the surface of discontinuity is strictly horizontal. The case just described, however, represents the simplest case under gravity. The case next in order of simplicity is the cylindrical surface of discontinuity. This is obtained by making a vertical cylindrical column of water to have different temperature from the rest of the liquid. To attain this experimentally, a thin hollow metal cylinder, open at both ends, is fitted with two glass rods, parallel to its axis and diametrically opposite at its upper end [fig. 3 (*b*)]. The two rods pass through two exact-fitting glass tubes which are rigidly clamped vertically. When the cylinder is raised by means of clockwork, the tubes serve as guides and prevent sideway displacements and rotation round its own axis. When the cylinder rests in water, the temperature of the liquid inside or outside may be decreased by means of ice or increased by a heating coil.

Two colour lines, diametrically opposite and parallel to the axis of the cylinder are painted on the surface of the cylinder before its insertion in the water. When the cylinder is raised up, the two coloured lines trace the form of the surface of discontinuity in a vertical section through the axis in the various stages of its growth.

The advantage of having two symmetrical colour lines instead of one is that we can trace the disturbing influence of factors other than the temperature difference, such as the initial state of motion of cold and warm water, any side way jerk caused by the shutter during removal, etc. However great might be the precaution, it is impossible to completely eliminate such disturbing factors.

In order to make comparative measurements the photographs were either of the same magnification or each had a glass scale photographed along with the phenomena.

During the withdrawal of the shutter, a certain amount of disturbance is produced in the liquid tending to increase the instability. This effect depends on the velocity of removal of the shutter and its thickness. When the shutter is withdrawn slowly (about 2 or 3 cm. per sec.) and steadily, the effect is very small. We would examine this effect at a later stage, and meanwhile proceed to give a discussion of the growth of the surface of discontinuity in the two cases on the assumption that this effect did not exist at all.

With the help of a heating coil of cylindrical or other shapes, it is possible to introduce a sudden discontinuity of temperature in still water if a strong electric current is momentarily passed through the coil. In such cases, the effect of drag due to shutter is absent, but the surface of discontinuity is of the convectional type. The motion which ensues is more complex than in the above examples and the surface of discontinuity rapidly develops into complicated patterns.

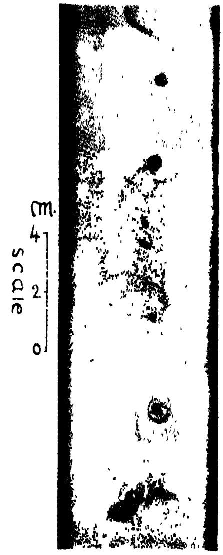


Fig. 26

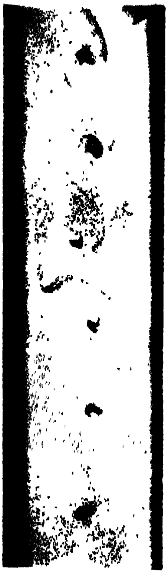


Fig. 27

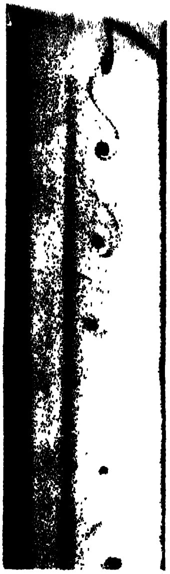


Fig. 28

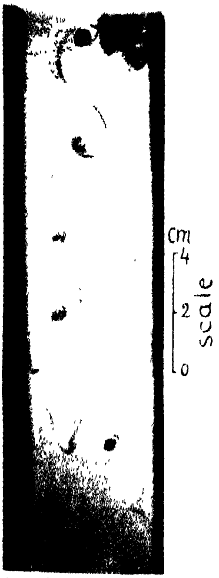


Fig. 29

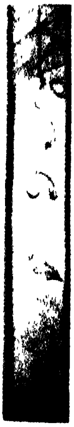


Fig. 30 2·9 c./s.

Fig. 31 4·2 c/s.

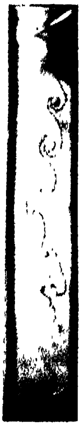


Fig. 32 5·1 c./s.

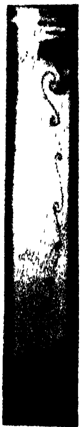


Fig. 33 7·1 c./s.

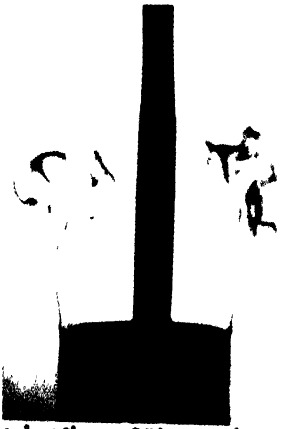


Fig. 34

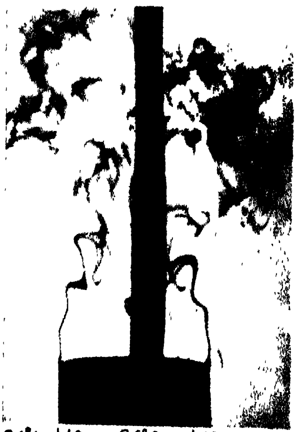


Fig. 35

Figs. 26-29. Showing the forms of the surface of discontinuity between two vertical rectangular columns of water having the initial temperature difference as indicated.

Figs. 30-33. Showing the influence of the partition between the columns on the production of vortices.

Figs. 34, 35. Showing the convection of a cylindrical sheath of warm water heated electrically.

4. *General discussion of the phenomena observed after a thermal discontinuity is introduced in still water.*

The growth of the surface of discontinuity which initially forms a vertical plane is shown in photographs, figs. 26, 27, 28 and 29 of Plate XI, and diagrammatically in fig. 4. The growth of a surface of discontinuity, which is initially cylindrical in shape, can be seen from the photographs, figs. 36, 37, 38, 39 of Plate XII and photographs, figs. 42, 43, 44 of Plate XIII. The original dimensions of the vortices in the tank can be obtained from the scale values shown against each figure.

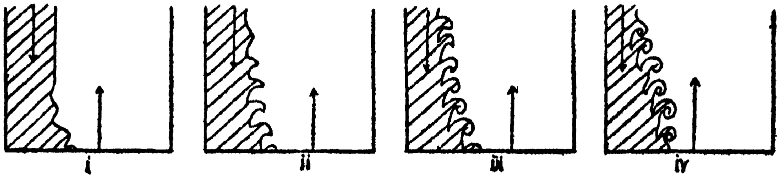


Fig. 4

It will be seen that in both cases the general nature of the phenomena is the same. As soon as the partition between the two columns of water having different temperatures is removed, the surface along which these two columns meet assumes a wave-form. As the thermal difference introduces a density difference, gravity produces motion in these two parts of the fluid. The warmer, that is to say, the lighter portion of the liquid travels upwards and the colder, that is to say, the denser portion of the liquid moves downwards. Gradually, the warm liquid rises over the cold liquid, the relative motion being a function of the difference of temperature between 'warm' and 'cold.' Finally the whole of the 'warm' fluid comes above the 'cold' and on account of the influence of the boundary the system undergoes a series of oscillations (fig. 5).

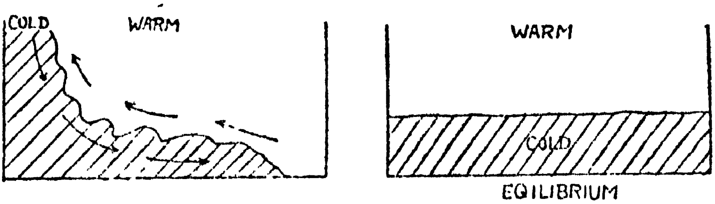


Fig. 5

At the surface of discontinuity, the two parts of the fluid are moving relatively in opposite directions (fig. 5). The surface of discontinuity is therefore initially one of the type discussed theoretically by Rosenhead, even though the subsequent motion, on account of the action of gravity is not identical. The growth of the surface of discontinuity, first into waves and subsequently into a series of vortices, follows closely the sequence deduced by Rosenhead from theoretical considerations (fig. 2).

It will be seen from the photographs that the crests and the troughs of the surface of discontinuity do not show equal development. In order to avoid confusion, we would call the protrusion of the surface of discontinuity towards the 'warm' a crest and that towards the 'cold' a trough. It will be seen that the crest assumes the form of a breaker at a very early stage and develops into a spiral vortex with rapidly increasing convolutions. The trough, on the other hand, shows very slow development. It assumes the shape of a breaker at a much later stage and rarely develops into a spiral-shaped vortex with a completed convolution. These features are strikingly demonstrated by figs. 42 and 43 of Plate XIII. Fig. 42 represents the case of a warm cylindrical column and fig. 43 that of a cold cylindrical column. The two cases, therefore, represent opposite conditions. The forms of the surface of discontinuity are consequently inverse to one another in the two photographs. Not only the crests, which have developed into spiral vortices, are in one case

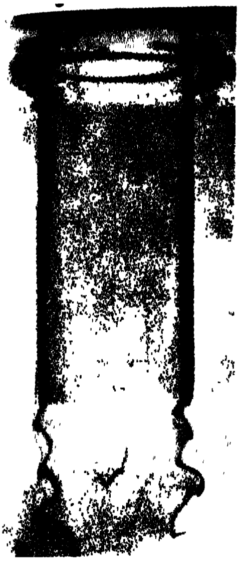


Fig. 36

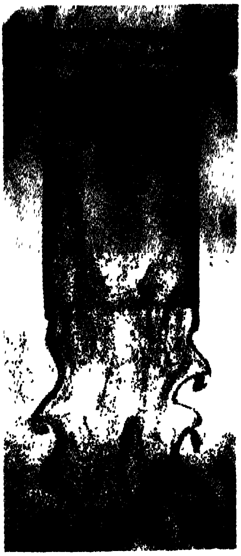


Fig. 37

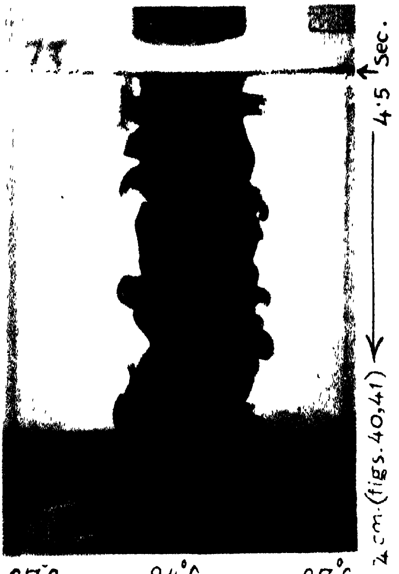


Fig. 40

scale 0 2 4 cm. (figs. 36-39)

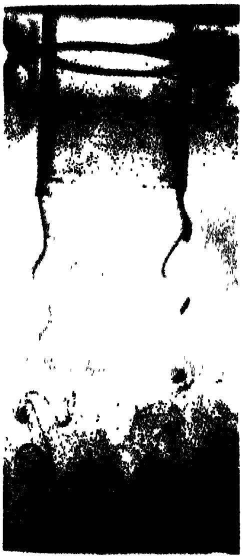


Fig. 38

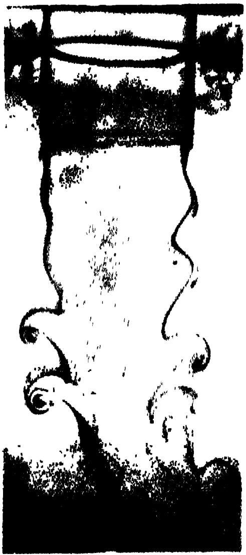


Fig. 39

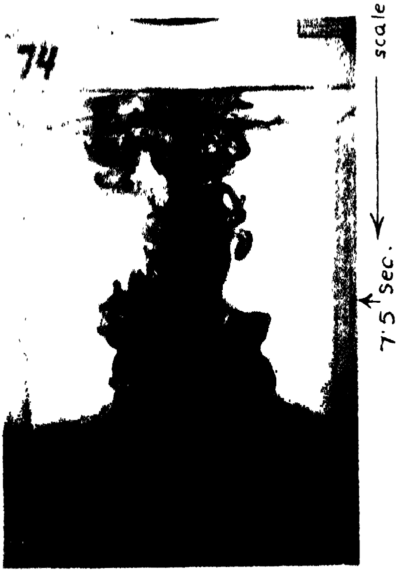


Fig. 41

Figs. 36-39. Showing the progressive development of cylindrical surface of discontinuity.

Figs. 49, 41. Showing the movement of the cylindrical surface of discontinuity.

inwards and in the other case outwards, but the rotations in the two cases are oppositely directed. Fig. 44 shows in a conspicuous manner the sequence of development of the crest and the trough. Owing to the finite time taken for the removal of the cylindrical shutter (about 2 secs.), as we go down the picture from above, the crests had more and more time to develop and consequently they show generally increasing number of convolutions. The troughs also show progressively increased development as we move down the picture, but not to the same extent as the crests. None of them in fact shows a complete convolution. These features can also be seen from the other photographs both for the plane and cylindrical discontinuities. We see also that *for any surface of discontinuity the crests and the troughs rotate in opposite directions.*

The growth of the surface of discontinuity in relation to the relative movement of the 'cold' or 'warm' liquid can be traced by colouring the entire liquid. This is shown in figs. 48, 49, 50, and 51 of Plate XIV for a rectangular column.

These are instantaneous photographs (exposure 1/25 sec.) taken at 2·5 secs., 7·5 secs., 12·5 secs. and 17·5 secs. respectively after the shutter began to be withdrawn. In fig. 48 we see how the cold column has started to sink down and how the surface of discontinuity has assumed a wavy form. In the next photograph (fig. 49) the column has sunk down still more. A certain amount of diffusion has occurred between the 'cold' and 'warm' liquid with the result that the surface of discontinuity is no longer as sharp nor the temperature contrast as great as in the first photograph. The waves have therefore increased in wave length as well as amplitude. In fig. 50, more diffusion has occurred, and the waves have still further increased in wave length and amplitude. This effect has been further accentuated in fig. 51. Similar effects associated with the sinking of a cylindrical column of water are shown by figs. 40 and 41 of Plate XII.

In order to determine the precise relationship between the directions of flow of 'warm' and 'cold' currents and the direction of rotation of the convolutions in the spiral vortices, it is necessary to emphasise that the spiral vortices represented by the crests have 'cold' cores and those represented by the troughs 'warm' cores. This is readily seen from the photographs. In a well-developed vortex formed by the crest the supply to the core or pole of the vortex can clearly be seen to come from cold water and in the case of vortex formed by the trough from the warm water.

At the surface of discontinuity, the warm and cold currents move relatively in opposite directions and thus produce at any point a turning moment (fig. 5). If we stand on a plane section parallel to the directions of these currents then the turning moment due to the opposite directions of motion may be clockwise or anti-clockwise according as we stand on one or the other face of the plane. If we stand on that face of the plane so that the turning moment is anti-clockwise then in the case of a vortex with a warm core we will have to move along the spiral in such a way that the core remains towards our left in order to arrive at the pole of the vortex and in the case of a vortex with a cold core we will have to move such that the core remains towards our right in order to arrive at the pole. These laws are in remarkable agreement with those which govern the directions of the wind in cyclones and anti-cyclones in the atmosphere. The turning moment due to the opposite directions of cold and warm currents appear to be equivalent to the part played by earth's rotation in atmospheric cyclones and anti-cyclones.

From measurement of photographs of the kind given in Plate XIV we can determine the horizontal velocity of the cold water at different times. The initial velocity is greater the greater is the difference of temperature at the surface of discontinuity. This will be clear from the data given in Table .I

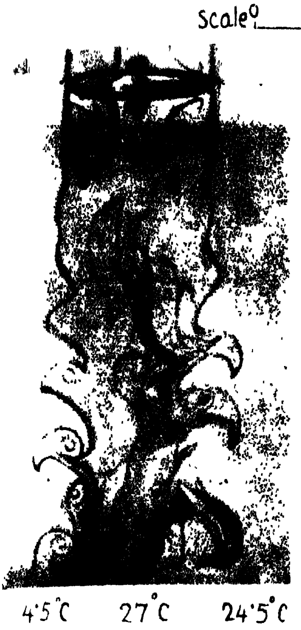


Fig. 42

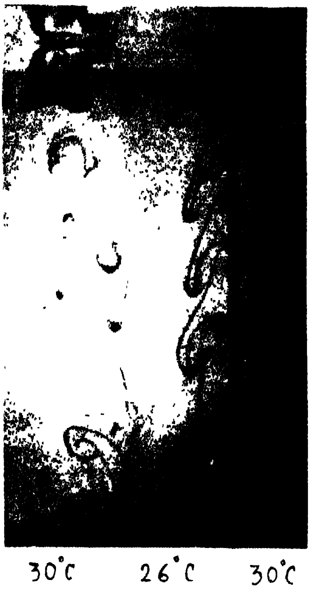


Fig. 43

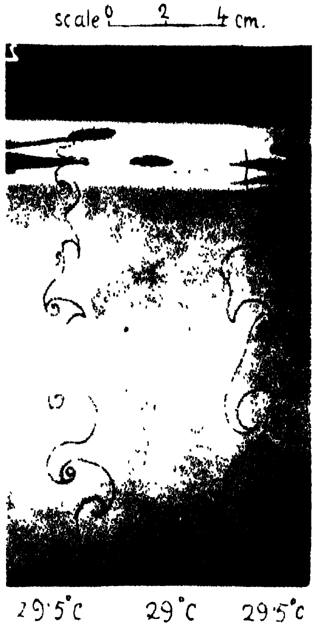
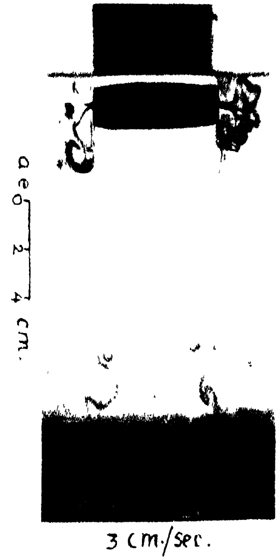
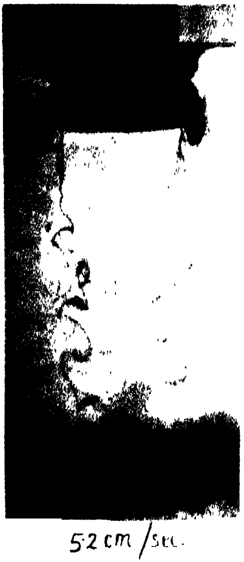
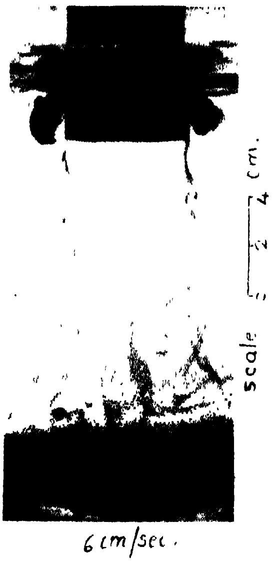


Fig. 44







Temperature difference at surface of discontinuity 3°C.

Fig. 45 Fig. 46 Fig. 47

Figs 42, 43 Showing the forms of the surface of discontinuity when the temperature of water inside the cylinder is greater and lower than that outside. (Note that the vortices rotate in opposite directions in the two cases.)

Fig. 44. Showing the form of the surface of discontinuity when the temperature difference is very small.

Figs 45-47. Showing the influence of cylindrical partition on the production of vortices

TABLE I.

Tank : Length 44·2 cm. × breadth 15·6 cm. × height 23·0 cm.

Cold column : Length 8·5 cm. × breadth 15·6 cm. × height 17·6 cm.

Warm column : Length 35·5 cm. × breadth 15·6 cm. × height 17·6 cm.

Temp. difference at surface of discontinuity 2°C.			Temp. difference at surface of discontinuity 4°C.		
Time (secs.) from start.	Hori. dist. moved (cm.).	Average velocity cm./sec.	Time (secs.) from start.	Hori. dist. moved (cm.).	Average velocity cm./sec.
2·5	3·58		2·5	3·4	
7·5	12·68	1·82	7·5	13·26	1·97
12·5	20·15	1·49	12·5	20·74	1·50
17·5	26·0	1·17	17·5	27·88	1·43
22·5	29·9	0·79	...	...	...

The velocity of sinking of a cold rectangular column, as deduced from figs. 48 and 49 of Plate XIV, is 1·8 cm./sec. This is the same as the horizontal velocity, as it obviously should be. The velocity of sinking of a cylindrical column, which is lower in temperature than the surrounding water by about 3°C, is about 3·3 cm./sec. (figs. 40 and 41 of Plate XII). The greater velocity in the case of the cylindrical column is due to the divergence at its base in *all* directions, as compared with the rectangular column which diverges only in one direction.

It is interesting to compare the above values with those which would be obtained for the motion in the early stage by a simple mathematical calculation. Owing to the density difference of cold and warm water, in any horizontal section there is a pressure difference at the surface of discontinuity and this tends to produce motion. The surface of discontinuity is not a mathematical plane. It is a layer of definite thickness approximately equal to double the amplitude of the waves, which we can take roughly to be a centimetre in the case under discussion. Let us consider, therefore, the motion of a layer of unit thickness, terminated by the discontinuous surface, of the cold column.

If ρ_1 is the density of cold water and ρ_2 the density of warm water and if at a depth h, the pressure is p_1 in the cold water and p_2 in warm water, we have

$$p_1 - p_2 = gh(\rho_1 - \rho_2)$$

Since the difference of pressure increases from a zero value at the surface to a maximum value at the bottom, the horizontal velocity of the layer will also, broadly speaking, increase from a zero value at the surface to a maximum value very close to the bottom. The motion of the layer may, therefore, be considered to be occurring under a mean value of the pressure difference acting over the entire column. The mean value of the pressure difference is

$$\tfrac{1}{2}gh\,(\rho_1 - \rho_2),$$

where h now denotes the total depth of the column.

A horizontal cylinder of unit length and of unit area at either end, over which the above pressure gradient is acting, will have an acceleration f, which is given by

$$\rho_1 f = \tfrac{1}{2}gh(\rho_1 - \rho_2),$$

$$\text{or,} \quad f = \tfrac{1}{2}gh(\rho_1 - \rho_2)/\rho_1.$$

We assume that the resistance to the motion of cold column follows a law similar to Stoke's law in the case of a sphere. According to this law the resistance experienced by a sphere moving with velocity v is $6\pi\mu va$, where μ is the coefficient of

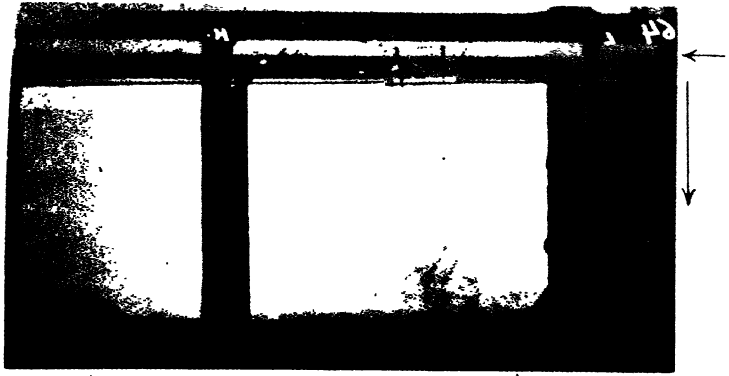


Fig 48.

2·5 Secs.

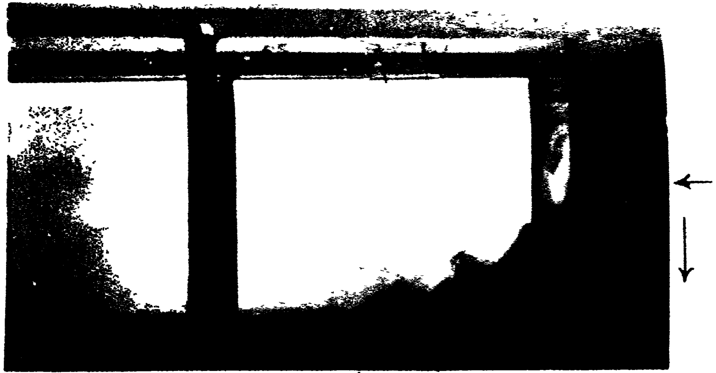


Fig. 49

7·5 Secs.

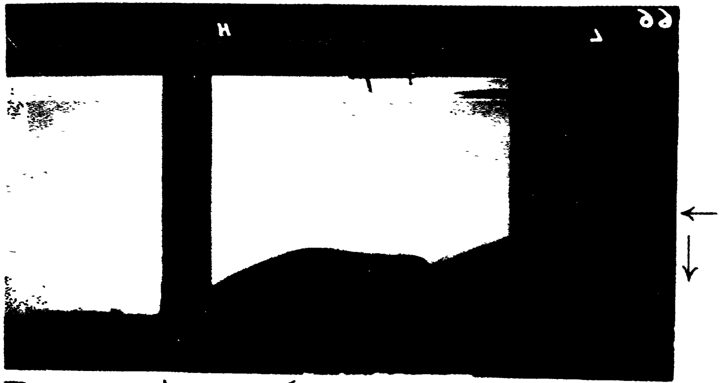


Fig. 50

12·5 Secs

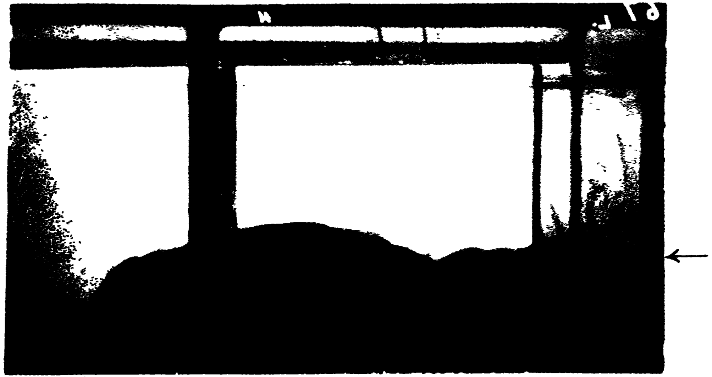


Fig. 51

17·5 Secs.

Showing the movement of surface of discontinuity, which was initially plane and vertical:

viscosity and a the radius of the sphere. If we consider the sphere to be equivalent to a flat plane transverse to the direction of motion, then we can express the resistance in the form

$$3\mu v \times \text{ circumference of the flat plane.}$$

For the cold column we will, therefore, assume that the resistance to its motion is equal to

$$3\mu v \times \text{length of the boundary of its transverse section,}$$

or, $\quad 3\mu vbh,$

where h is the depth of water and b is the breadth of tank. It is not a rigorously correct assumption, but since the cold column moves with a curved surface it appears to be a plausible assumption. The equation of horizontal motion of the layer can therefore be expressed in the form

$$\frac{dv}{dt} = f - kv,$$

where $\quad k = 3\mu hb.$

Integrating, we get

$$t = \frac{1}{k} \log \frac{f}{f-kv}, \quad \text{since } v = 0 \text{ when } t = 0,$$

or, $\quad v = \frac{f}{k}(1-e^{-kt}).$

As f is not a constant but decreases with distance (or time), this formula can be considered to be approximately true only for the early stage of the motion.

(1) Now in the first case (Table I), we have

$$t_1 = 24°c, \quad t_2 = 26°c, \quad h = 17{\cdot}6cm., \quad b = 15{\cdot}6cm.$$

Therefore

$$f = \tfrac{1}{2}gh\frac{\rho_1-\rho_2}{\rho_1}$$

$$= \frac{981 \times 17{\cdot}6 \times ({\cdot}99681 - {\cdot}99626)}{2 \times {\cdot}99681}$$

$$= 4{\cdot}8 cm./sec.^2$$

$$k = 3 \times {\cdot}01 \times (2 \times 17{\cdot}6 + 2 \times 15{\cdot}6) = 1{\cdot}99 \text{ C.G.S.}$$

$$v = \frac{4{\cdot}8}{1{\cdot}99}\left(1 - e^{-1{\cdot}99}\right) = 2{\cdot}1 cm./sec. \text{ (after 1 sec.).}$$

(2) In the second case (Table I),

$t_1 = 23°c$, $t_2 = 27°c$, $h = 17{\cdot}6 cm.$, $b = 15{\cdot}6 cm.$

Therefore

$$f = \tfrac{1}{2}gh\frac{\rho_1-\rho_2}{\rho_1}$$

$$= 981 \times 8{\cdot}8 \times \frac{{\cdot}99756 - {\cdot}99653}{{\cdot}99756}$$

$$= 8{\cdot}9 cm./sec.^2$$

$$k = 1{\cdot}99 \text{ C.G.S.}$$

$$v = 3{\cdot}8 cm./sec. \text{ (after 1 sec.).}$$

We thus get in the two cases the velocities of 2·1 cm./sec. and 3·8 cm./sec. in the early stage of the motion against the observed values of about 1·82 cm./sec. and 1·97 cm./sec. respectively. The discrepancies are obviously due to the rough approximation made both in the assumption and the calculation. The quantities are, however, roughly of the order actually observed.

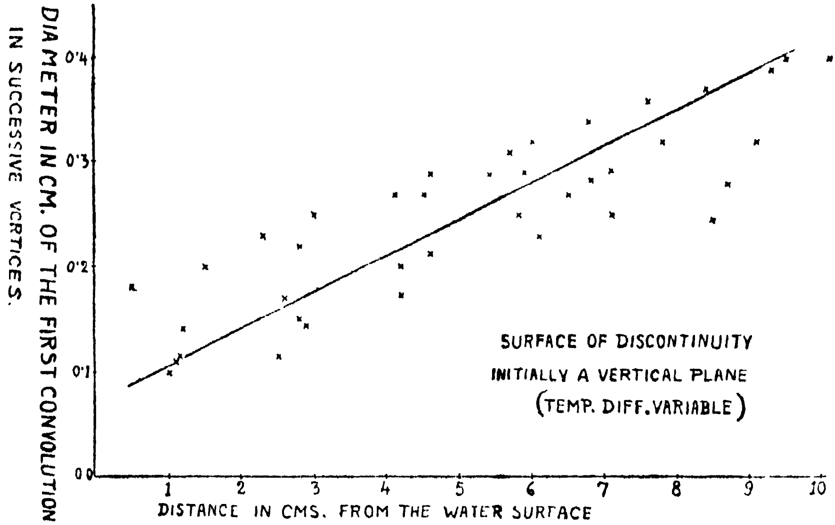


Fig 6

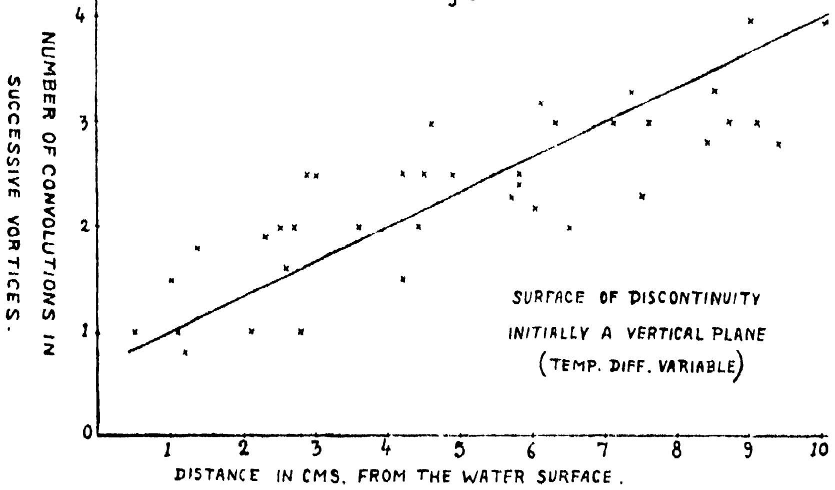


Fig 7

The statistical laws of the growth of vortices in the case of a surface of discontinuity, which is initially a vertical plane, have been shown graphically in figs. 6 and 7. The distances and diameters given in these figures are from the photographs, which were all of the same magnification. They should be multiplied by 1·8 in order to get the actual values. In fig. 6 the diameter of the first convolution in the successive vortices from the water surface downwards has been plotted against their depth from the water surface. Since the vortex lower down in the liquid had greater time to develop than the one higher up, we can conclude from this curve that in general a vortex increases in diameter with time. The large scatter in the observational points is obviously due to the fact that all the observed cases, irrespective of the actual temperature difference at the surface of discontinuity, have been included in this curve. We will find later on that the feature shown by this curve is covered by the general law that a growth of the vortex is always associated with an increase in the amplitude of the surface of discontinuity.

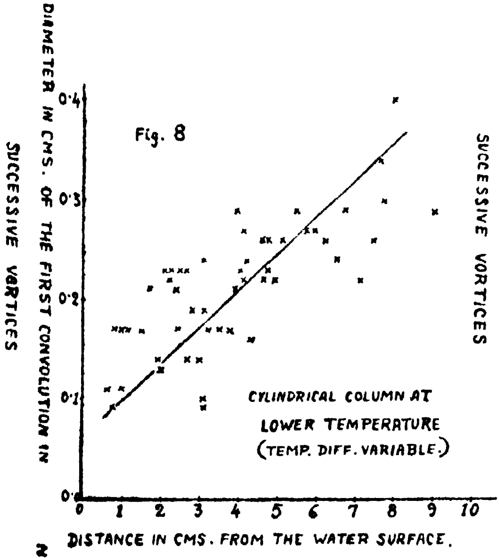


Fig. 8

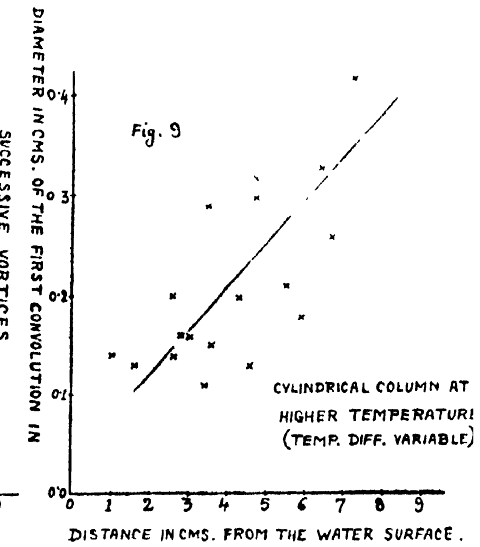


Fig. 9

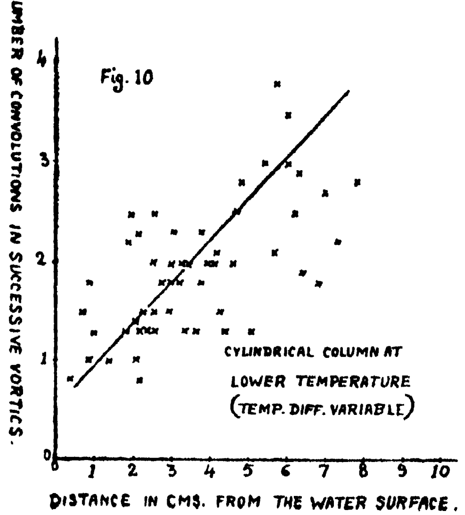


Fig. 10

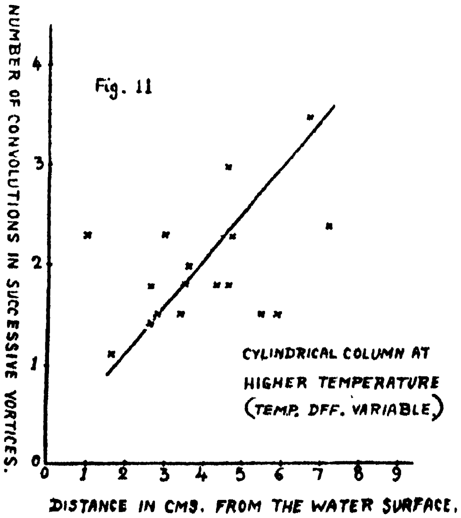


Fig. 11

In fig. 7, the number [8] of convolutions of the successive vortices have been plotted against the depths of the vortices below the water surface. Here, too, we see that in general there is an increase in the number of convolutions with the growth of a spiral vortex. The large scatter in the curve is due, as in the previous case, to the inclusion of all cases irrespective of the actual difference of temperature at the surface of discontinuity.

The corresponding cases for a cylindrical discontinuity, the cylindrical column being either at higher or lower

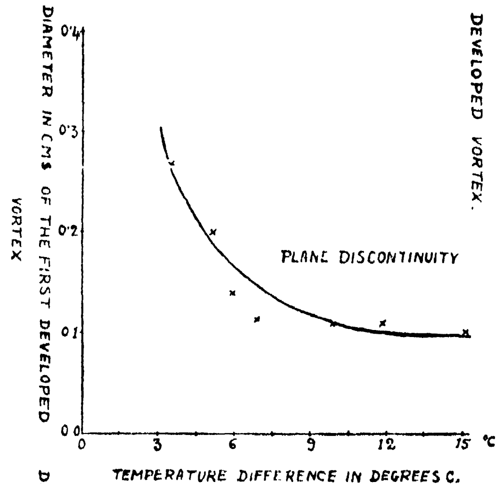


Fig. 12

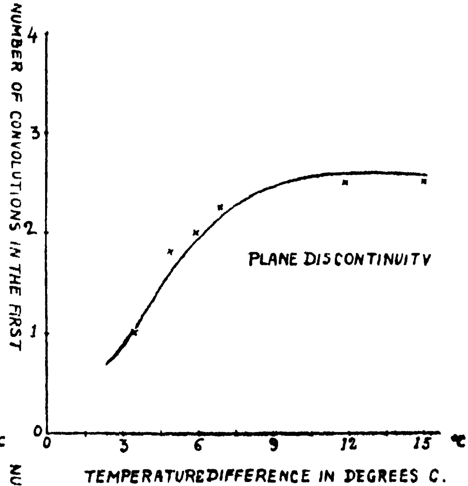


Fig. 14

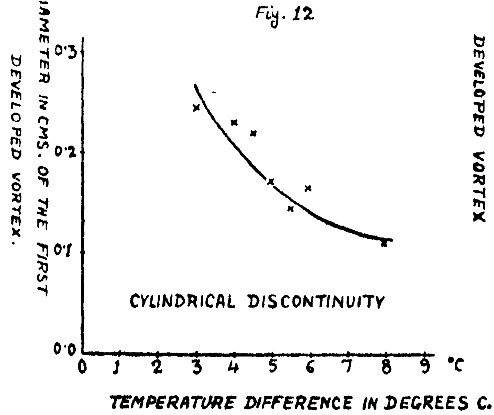


Fig. 13

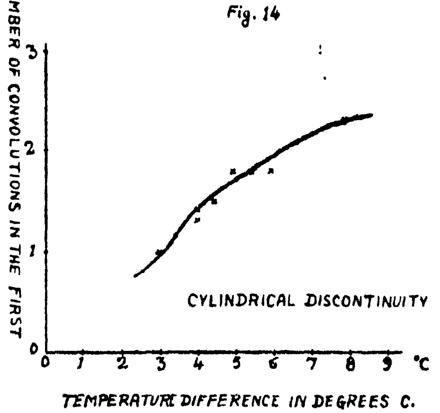


Fig. 15

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[8] If $2\pi n$ is the total angle subtended at its centre by a spiral vortex, then n denotes its number of convolutions.

temperatures than the surrounding water, have been given in figs. 8, 9, 10 and 11. The distances and the diameters given in these figures have also been taken from the photographs. They should be multiplied by 1·4 in order to get the actual values. All these curves show as in the case of a plane discontinuity that the dimensions as well as the number of convolutions in a spiral vortex increase with time. The scatter is due to the same cause as before.

The growth of vortices in individual cases and for various differences of temperature at the surface of discontinuity can be seen from the data given in Tables II and III.

The general results which can be deduced from the data given in Tables II and III have been shown graphically in figs. 12, 13, 14 and 15. In fig. 12, the diameter (actual, 1·8 times) of the first vortex in the case of plane discontinuities counted from surface downwards has been plotted against the initial difference of temperature at the surface of discontinuity. It will be seen that the diameter of a vortex undergoes an increase with decrease in the difference of temperature at the surface of discontinuity. The diameter increases rather slowly as the temperature difference is reduced to 5°C, but for smaller temperature difference the diameter increases very rapidly. The curve in fact has a tendency to become asymptotic to the diameter-axis. The same feature is shown by the curve in fig. 13 for a cylindrical discontinuity. Here, too, we see that for smaller difference of temperature at the surface of discontinuity, the diameter (actual, 1·4 times) of the vortex increases very rapidly.

On the other hand, the larger the initial difference of temperature at the surface of discontinuity, the more rapidly a vortex grows. This is readily seen from figs. 14 and 15. In fig. 14, the number of convolutions in the first developed vortex in the case of a plane discontinuity, counted from the water surface downwards, has been plotted against the difference of temperature at the surface of discontinuity. The

TABLE II.

Plane Discontinuity.

Tank : Length 44·2 cm. × breadth 15·6 cm. × height 23·0 cm.
Cold column : Length 8·5 cm. × breadth 15·6 cm. × height 19·2 cm.
Warm column : Length 35·5 cm. × breadth 15·6 cm. × height 19·2 cm.
Thickness of shutter : 1·6 mm.

The figures in columns 3, 4 and 5 are from the photographs. They should be multiplied by 1·8 to convert them to actuals.

Photo number.	Diff. in temps. °C.	Dist. from the water surface, of successive vortices (×1·8 cm.).	Diam. of first convolution in successive vortices (×1.8 cm.).	**Average diam.** (×1.8 cm.).	No. of convolutions ($2\pi \times n$) n.	No. of convolutions of the first developed vortex ($2\pi \times n$) n.
1	3·5	2·6	0·17	0·30	1·0	1·0
		4·1	0·27		2·0	
		5·4	0·29		2·5	
		6·8	0·34		3·0	
		7·8	0·32		3·25	
		9·3	0·39		4·00	
2	5·0	1·5	0·20	0·27	1·75	1·75
		3·0	0·25		2·50	
		4·5	0·27		2·50	
		5·9	0·28		2·40	
		7·6	0·29		3·00	
		9·1	0·32		3·00	
3	6·0	1·2	0·14	0·29	1·50	2·00
		2·8	0·22		2·00	
		4·6	0·29		2·00	
		6·0	0·32		2·16	
		7·6	0·36		2·25	
		9·5	0·40		2·75	
4	7·0	1·2	0·11	0·19	0·75	2·25
		2·8	0·15		1·00	
		4·2	0·17		1·50	

TABLE II—*Continued.*

Plane Discontinuity.

Tank : Length 44·2 cm. × breadth 15·6 cm. × height 23·0 cm.
Cold column : Length 8·5 cm. × breadth 15·6 cm. × height 19·2 cm.
Warm calumn : Length 35·5 cm. × breadth 16·6 cm. × height 19·2 cm.
Thickness of shutter : 1·6 mm.

The figures in columns 3, 4 and 5 are from the photograghs. They should be multiplied by 1·8 to convert them to actuals.

Photo number.	Diff. in temps. °C.	Dist. from the water surface, of successive vortics (×1·8 cm.).	Diam. of first convolution in successive vortics (×1·8 cm.).	Average diam. (×1·8 cm.).	No. of convolutions (2π × n) n.	No. of convolutions of the first developed vortex (2π × n) n.
		5·7	0·17		2·25	
		7·1	0·25		3·00	
		8·7	0·28		3·00	
5	10·0	1·1	0·11	0·25	1·0	1·62
		2·6	0·17		1·62	
		4·2	0·20		2·50	
		5·3	0·25		2·50	
		6·8	0·28		...	
		8·4	0·37		2·75	
		10·1	0·40		4·00	
6	12·0	2·5	0·11	0·14	2·00	2·50
		4·2	0·17		2·50	
7	13·0	0·5	0·18	0·23	1·0	1·85
		2·3	0·23		1·85	
		4·1	0·24		1·9	
		6·5	0·27		2·00	
8	15·4	·6	0·10	0·20	1·50	2·50
		2·5	0·14		2·50	
		4·2	0·21		3·00	
		5·7	0·23		3·15	
		8·1	0·24		3·25	
		10·6	0·28		3·75	

TABLE III.

Cylindrical Discontinuity.

Tank : Length 19·3 cm. × breadth 17·0 cm. × height 20·0 cm.
Depth of water : 17·5 cm.

The figures given in columns 8, 9 and 10 are from the photographs. They should be multiplied by 1·4 to convert them to actuals.

Photo No.	Dim. of cylinders (cm.).			Temp. °C.		Diff. in Temp. °C.	Dist. from water surface (×1.4 cm.). (Both rows).	Diam. of first convolution (×1·4 cm.).	Aver. diam. (×1·4 cm.).	No. of convolutions (2π×n) n.	No. of convolutions in the first developed vortex. n.
	Radius	Length	Thickness	Inside	Outside						
9	2·3	20·0	0·14	27·0	27·5	0·5	2·3	0·22	0·25	1·5	...
							2·6	0·23		1·3	
							6·8	0·29		1·8	
10	,,	,,	,,	27·5	28·5	1·0	1·1	0·17	0·21	1·3	1·3
							2·4	0·17		1·5	
							4·7	0·26		2·5	
							6·3	0·26		2·9	
11	,,	,,	,,	23·0	26·0	3·0	1·0	0·17	0·22	1·1	1·1
							3·1	0·24		2·3	
							4·2	0·24		...	
12	,,	,,	,,	26·0	30·0	4·0	1·9	0·14	0·20	2·5	
							2·4	0·21		2·3	
							4·9	0·24		2·5	
13	,,	,,	,,	21·0	25·0	4·0	1·5	0·17	0·22	1·0	1·4
							2·1	0·23		1·4	
							3·1	0·19		1·5	
							3·9	0·27		2·3	
14	,,	,,	,,	26·0	30·0	4·0	1·9	0·13	0·23	2·3	
							2·8	0·19		1·8	

TABLE III—*Continued.*

Cylindrical Discontinuity.

Tank : Length 19·3 cm. × breadth 17·0 cm. × height 20·0 cm.
Depth of water : 17·5 cm.

The figures given in columns 8, 9 and 10 are from the photographs. They should be multiplied by 1·4 to convert them to actuals.

Photo No.	Dim. of cylinders (cm.).			Temp. °C.		Diff. in Temp. °C.	Dist. from water surface (×1·4 cm.). (Both rows).	Diam. of first convolution (×1·4 cm.).	Aver. diam. (×1·4 cm.).	No. of convolutions (2π × n). n.	No. of convolutions in the first developed vortex. n.
	Radius	Length	Thickness	Inside	Outside						
							4·0	0·23		2·0	
							5·1	0·26		...	
							5·7	0·27		...	
							6·5	0·24		1·9	
							7·4	0·26		2·2	1·5
15	3·2	23·0	0·03	26·0	30·5	4·5	0 8	0·09	0·15	1·5	
							2·7	0·14		2·5	
							7·1	0·22		2·7	
16	2·3	20·0	0·14	22·0	27·0	5·0	3·5	0·17	0·22	1·3	1·8
							3·9	0·21		1·8	
							4·7	0·23		2·0	
							6·2	0·26		2·5	
17	,,	,,	,,	21·0	26·0	5·0	0·8	0·17	0·23	2·5	2·5
							1·7	0·21		1·3	
							2·5	0·23		2·3	
							4·1	0·27		1·5	
							5·9	0·27		3·5	
18	,,	,,	,,	21·0	26·5	5·5	3·0	0·14	0·21	1·8	1.8
							3·4	...		2·0	
							5·9	0·27		3·0	

TABLE III—*Continued.*

Cylindrical Discontinuity.

Tank : Length 19·3 cm. × breadth 17·0 cm. × height 20·0 cm.
Depth of water : 17·5 cm.

The figures given in columns 8, 9 and 10 are from the photographs. They should be multiplied by 1·4 in order to convert them to actuals.

Photo No	Dim. of cylinders (cm.).			Temp. °C.		Diff. in Temp. °C.	Dist. from water surface (× 1·4 cm.). (Both rows).	Diam. of first convolutions (× 1·4 cm.).	Aver. diam. (× 1.4 cm.).	No. of convolutions (2π × n). n.	No. of convolutions in the first developed vortex. n.
	Radius	Length	Thickness	Inside	Outside						
19	2·3	20·0	0·14	20·0	26·0	6·0	2·1	...	0·22	1·0	...
							3·1	0·09		2·0	
							4·3	0·16		2·1	
							5·6	0·21		3·8	
							6·4	0·23		...	
							7·95	0·40		...	
20	,,	,,	,,	20·0	26·0	6·0	0·6	0·11	0·21	0·8	1·3
							2·4	0·17		1·3	
							4·9	0·22		...	
							7·6	0·32		2·8	
21	,,	,,	,,	20·0	26·0	6·0	3·8	0·17	0·25	...	...
							4·9	0·24		...	
							5·4	0·29		3·0	
							7·7	0·30		...	
22	3·2	23·0	0·03	24·0	30·0	6·0	3·1	0·10	0·21	0·8	1·8
							3·3	0·17		1·8	
							4·1	0·24		1·3	
							4·6	0·26		...	
							7·0	0·29		...	

TABLE III—*Continued.*

Cylindrical Discontinuity.

Tank : Length 19·3 cm. × breadth 17·3 cm. × height 29·0 cm.

Depth of water : 17·5 cm.

The figures given in columns 8, 9 and 10 are from the photographs. They should be multiplied by 1·4 in order to convert them to actuals.

Photo No.	Dim. of cylinders (cm.).			Temp. °C.		Diff. in Temp. °C.	Dist. from water surface (×1·4 cm.). (Both rows).	Diam. of first convolutions (×1·4 cm.).	Aver. diam. (×1·4cm.).	No. of convolutions (2π × n). n.	No. of convolutions in the first developed vortex. n.
	Radius	Length	Thickness	Inside	Outside						
23	,,	,,	,,	22·0	30·0	8·0	1·0	0·11	0·14	1·8	2·3
							2·0	0·13		1·5	
							3·2	0·17		2·3	
24	2·3	20·0	0·14	26·0	25·0	−1·0	1·6	0·13	0·16	1·1	1·1
							2·6	0·14		1·8	
							2·8	0·16		1·5	
							3·6	0·15		2·0	
							5·5	0·21		1·5	
							5·9	0·18		1·5	
25	,,	,,	,,	26·5	24·5	−2·0	1·0	0·14	0·17	2·3	2·3
							3·0	0·16		2·3	
							4·6	0·13		3·0	
							6·7	0·26		3·5	
26	,,	,,	,,	27·0	24·5	−2·5	3·4	0·11	0·28	5	1·5
							4·3	0·20		1·8	
							4·6	0·32		1·8	
							6·4	0·33		1·8	
							7·2	0·42		2·4	
27	,,	,,	,,	27·5	24·5	−3·0	2·6	0·20	0·26	1·4	1·8
							3·5	0·29		1·8	
							4·7	0·30		2·3	

number of convolutions in a vortex is a measure of its growth. The curve vividly presents to the eye that the number of convolutions at first increases rapidly and then slowly with increase in the difference of temperature at the surface of discontinuity. The growth of a vortex, therefore, occurs more quickly the greater is the difference of temperature at the surface of discontinuity. Similar feature is shown by the curve in fig. 15 for a cylindrical discontinuity.

We deduce from the above observations the following two important laws :—

(1) The smaller the difference of temperature at the surface of discontinuity the greater is the diameter of the vortex. When the difference of temperature approaches zero, the diameter asymptotically increases to an infinitely large value.

(2) The larger the difference of temperature at the surface of discontinuity the more rapidly a vortex grows.

We will see from the further observations of temperature discontinuities in moving liquids which we will describe in Part II that these laws are of very general application.

We have seen that each crest of a surface of discontinuity develops into a spiral vortex ; the troughs gradually assume the form of a breaker but seldom develop into a spiral vortex. The distance between successive vortices formed by the crests is therefore equivalent to the wave-length of the surface of discontinuity. If a symmetrical line is drawn through the surface of discontinuity so that the crests and troughs lie on either side of this line, then we can take either the distance of the peak of each trough from this line or the diameter of the complete vortex formed by each crest as the amplitude of the surface of discontinuity, the latter being just separated out by the symmetrical line. To indicate the manner how the wave-length and amplitude of a surface of discontinuity vary along its length and how they depend on the temperature difference, we have given in Table IV (*a*) and (*b*) the results obtained from an analysis of a few typical photographs for plane and cylindrical discontinuities. Under the experimental conditions, a surface of discontinuity seldom grows purely under the influence of temperature difference. The initial state of motion of warm and cold water and other uncontrollable factors exercise a disturbing influence on the pattern. The values of wave-length and amplitude do not, therefore, represent those that would have been obtained under ideal conditions. They can, however, be considered to represent, on the average, the order of quantities correctly.

We have already noted that there is a progressive increase in the growth of vortices from surface downwards, the lowest one is more developed than the one next above and so on. We see from Table IV (*a*) and (*b*) that in the case of an individual surface of discontinuity, both the wave-length and amplitude undergo, in general, an increase from surface downwards in consonance with this growth. When we consider the different cases collectively we notice that as the temperature difference at the surface of discontinuity is increased, the wave-length does not undergo much variation but the amplitude undergoes a rapid decrease.

If the trough had developed to the same extent as the crest, then the crest vortices and the trough vortices could be regarded as forming a double row of vortices. Even though the pattern does not quite correspond to the Kármán vortex street, we can still consider the crest vortices and the ill-developed trough vortices to be forming a double row. We then find [Table IV (*a*) and (*b*)] that the ratio of h, the distance between the poles of the two rows of vortices (which is equal to the amplitude), to λ, the distance between successive crest vortices (which is equal to wave-length) has very nearly the value 0·283 which Kármán found for his stable rows of vortices.

The ratio, $h:\lambda$, appears to undergo a slight decrease with increase in temperature at the surface of discontinuity.

TABLE IV (*a*).

Plane Discontinuity.

The figures given in columns 6, 7, 8 and 9 are from the photographs. They should be multiplied by 1·8 in order to convert them to actuals.

Photo No.	Temp. °C		Temp. diff. °C.	Vortex numbers counted from surface downwards.	Wave-length : dist. between successive vortices (× 1·8 cm.).		Amplitude (× 1·8 cm.).		$\frac{h}{\lambda}$
	Cold	Warm			Observed	Mean λ	Observed	Mean *h*	
28	28·5	32·0	3·5	1	1·5		0·4		
				2	1·3		0·5		
				3	1·1		0·6		
				4	1·1		0·6		
				5	1·6		0·6		
				6		1·4	0·7	0·6	0·43
29	28·0	33·0	5·0	1	1·5		0·3		
				2	1·5		0·4		
				3	1·5		0·4		
				4	1·7		0·4		
				5	1·5		0·55		
				6		1·5	0·4	0·4	0·26
30	26·0	32·0	6·0	1	1·7		0·3		
				2	1·7		0·4		
				3	1·4		0·45		
				4	1·6		0·5		
				5	1·9		0·4		
				6		1·7	0·5	0·4	0·23
31	25·5	32·5	7·0	1	1·5		0·25		
				2	1·5		0·3		

TABLE IV (*a*)—*Continued.*

Plane Discontinuity.

The figures given in columns 6, 7, 8 and 9 are from the photographs. They should be multiplied by 1·8 in order to convert them to actuals.

Photo No.	Temp. °C.		Temp. Diff. °C	Vortex numbers counted from surface downwards.	Wave-lengths: dist. between successive vortices (×1·8 cm.).		Amplitude (×1·8 cm.).		$\frac{h}{\lambda}$
	Cold	Warm			Observed	Mean λ	Observed	Mean *h*	
				3	1·3		0·3		
				4	1·6		0·4		
				5	1·6		0·4		
				6		1·5	0·5	0·4	0·26
32	22·5	32·5	10·0	1	1·7		0·2		
				2	1·5		0·3		
				3	1·2		0·5		
				4	1·7		0·4		
				5	1·7		0·4		
				6		1·6	0·6	0·4	0·25
33	20·0	33·0	13·0	1	1·8		0·3		
				2	1·8		0·4		
				3	2·5		0·4		
				4	1·6		0·4		
				5	2·2		...		
				6		2·0	...	0·4	0·20
34	17·8	33·2	15·4	1	2·0		0·25		
				2	1·8		0·3		
				3	1·5		0·4		
				4	2·5		0·4		
				5	2·4		0·4		
				6		2·0	0·4	4·0	0·20
							Mean		**0·26**

TABLE IV (*b*).

Cylindrical Discontinuity.

The figures given in columns 6, 7, 8 and 9 are from the photographs. They should be multiplied by 1·4 in order to convert them to actuals.

Photo No.	Temp. °C.		Temp. diff. °C.	Vortex numbers counted from surface downwards.	Wave-length: dist. between successive vortices (×1·4 cm.).		Amplitude (×1·4 cm.).		$\frac{h}{\lambda}$
	Cold	Warm			Observed	Mean λ	Observed	Mean h	
35	27·5	28·5	1·0	1	1·3		0·6		
				2	2·2		0·55		
				3	1·7		0·5		
				4		1·7	0·7	0·6	0·35
36	23·0	26·0	3·0	1	1·0		0·35		
				2	1·4		...		
				3	1·2		0·5		
				4		1·2	0·5	0·5	0·42
37	26·0	30·0	4·0	1	1·0		0·35		
				2	1·2		0·4		
				3	1·1		0·4		
				4	0·8		0·3		
				5	0·7		0·4		
				6	1·0		0·4		
				7	1·1		0·5		
				8		1·0	...	0·4	0·40
38	21·0	26·0	5·0	1	0·9		0·3		
				2	1·6		0·5		
				3	1·6		0·5		
				4	1·8		...		
				5		1·5	0·5	0·5	0·33
39	24·0	30·0	6·0	1	0·8		0·2		
				2	1·5		0·2		
				3	1·4		0·3		
				4		1·2	0·3	0·3	0·25

Mean ... 0·35

5. *Effect of initial conditions, boundaries, etc., on subsequent development of vortices.*

It has already been stated that a disturbing influence is produced by shutters during their removal tending to increase the instability of the surface of discontinuity. To determine the effect of the drag produced by the motion of a shutter, it was removed with different velocities, and the surfaces of discontinuity, in which the temperature difference was the same, photographed immediately after removal. In order to have a constant velocity during removal, the shutter was raised up by clockwork, fitted with a governor, with the aid of a ball-bearing pulley. The velocity was measured by noting the time required for the shutter to travel a fixed distance.

It is found that even if there is no temperature difference a train of vortices will develop in the wake of the shutter provided its velocity is not less than 2 cm. per second. When, however, there is a temperature discontinuity, the vortices would appear even if the shutter moves with very slow velocity. If the difference of temperature is kept constant and if the shutter is withdrawn with different velocities, it is found that the greater the velocity of shutter the more rapidly the vortices develop. At the same time the amplitude and wave-length undergo a decrease, that is to say, the vortices become smaller in dimensions and a large number of them appear within the same space. This is clearly exhibited by figs. 30, 31, 32 and 33 of Plate XI for a plane discontinuity and by figs. 45, 46 and 47 of Plate XIII for a cylindrical discontinuity. In figs. 30, 31, 32 and 33 of Plate XI, the velocities of removal of shutter were 2·9 cm./sec., 4·2 cm./sec., 5·1 cm./sec., and 7·1 cm./sec., respectively. They show a progressive decrease both in the amplitude and wave-length of the surface of discontinuity.

The same features are shown by figs. 45, 46 and 47 of Plate XIII. The actual reduction in amplitude and wave-length of the surface of discontinuity due to increased speed of the shutter has been given in Table V.

In order to determine the effect of thickness, shutters of thickness 0·3 mm. and 1·4 mm. were tried and within this small range no appreciable effect could be traced on the development of vortices. It was found, however, that when the shutter has very large thickness, say of the order of 0·5 cm., it has great disturbing influence on the surface of discontinuity. The vortices would not develop in the symmetrical pattern, nor would they assume the neat spiral forms usually obtained with very thin shutters ; they would in fact become all diffused. We always used therefore shutters of very small thickness in studying the behaviour of the surface of discontinuity in water initially at rest.

If a fixed heating coil of cylindrical shape is inserted in water and if the temperature of contiguous water is suddenly raised by passing through the coil a strong electric current momentarily (for about a second) then we avoid the use of a shutter and introduce a temperature discontinuity before any appreciable motion ensues. By adopting this method we do not make a definite mass of water of some simple geometrical shape acquire a uniform but different temperature from that of the surrounding water. We merely make the layer of water next to the electrically heated surface to have a non-uniform but different temperature from that of the surrounding liquid. This layer being lighter travels upwards as a discontinuous mass and traces a surface of discontinuity roughly of the kind traced by a jet.

Some experiments were made with a hollow clyindrical heater such as are now manufactured on a commercial scale for heating water and given the name "eltron." When a colour line is made to trace the up-rising surface of discontinuity, it is seen to assume a wavy form and end as a spiral in

TABLE V.

Plane discontinuity: Temp. diff. 1°C.
Tank: Length 44·2 cm. × breadth 15·6 cm. × height 23·0 cm.
Cold column: Length 8·5 cm. × breadth 15·6 cm. × height 17·7 cm.
Warm column: Length 35·5 cm. × breadth 15·6 cm. × height 17·7 cm.

The figures given in columns 3 and 4 are from the photographs. They should be multiplied by 2·4 to convert them to actuals.

Photograph No.	Velocity of removal of shutter. cm./sec.	Amplitude (×2·4 cm.).	Wave-length. (×2·4 cm.).
40	2·93	0·3	1·5
		0·4	1·6
		0·4	1·6
		0·4	0·9
		0·5	
41	4·20	0·25	1·0
		0·3	1·0
		0·35	1·2
		0·3	1·1
		0·3	
42	5·13	0·2	0·8
		0·2	0·9
		...	0·8
		...	1·0
		...	0·8
43	7·00	0·1	
		0·15	0·7 (average)
		...	
		...	

Cylindrical discontinuity: Temp. diff. 3°C.
Tank: Length 19·8 cm. × breadth 17·0 cm. × height 20·0 cm.
Depth of water: 17·5 cm.; Diameter of Cylinder: 6·4 cm.

44	3·00	0·3	1·5
		0·3	1·0
		0·4	0·9
			0·9
45	5·25	0·2	0·8
		0·2	1·2
		0·3	0·9
		0·3	
46	6·00	0·1	0·6
		0·1	0·7
		0·2	0·6
		0·2	0·7
		...	0·9
		...	0·9

the early stage, like that in the case of a jet (fig. 34 of Plate XI). In the later stage, that is to say, with further travel upwards, the end becomes diffused (fig. 35 of Plate XI). The form of the surface of discontinuity upto a certain height above the cylinder is very similar to that obtained in the early stage with cylindrical shutter by the method previouly described.

In experiments with plane shutters, the depth of the liquid was about 19 cm. and with cylindrical shutters, about 18 cm. If we make the depth of the liquid larger then we increase the pressure difference in the lower part of the surface of discontinuity. This would make the relative velocity between cold and warm water larger and would bring a thicker layer of each under mutual action. We would therefore expect theoretically that the vortices in the lower part would be bigger in dimensions. This is what experiments also indicate, as can be seen from the figures given in Table VI.

TABLE VI.

Cylindrical Discontinuity.

Photograph number.	Temperature.		Length of cylindrical discontinuity, cm.	Successive vortices.	
	Inside °C.	Outside °C.		Wave-length, cm.	Amplitude, cm.
47	26·0	30·5	17·5	1·52 1·86	0·54 0·72 0·75
48	26·0	30·5	30·0	3·40 3·06 2·38 3·74	0·85 1·02 1·02 1·36 1·36

PART II.

Thermal Discontinuity in a Moving Liquid.

6. *Experimental arrangement for introducing a thermal discontinuity in moving liquids.*

We can generate a surface of discontinuity by making a current of water at a certain temperature flow through water at another temperature, the latter being either stationary or in a state of motion. When this method is adopted it is impossible to avoid the effect of divergence or convergence of the surface of discontinuity. What we mean by this statement is explained by figs. 52, 53, 54 and 55 of Plate XV. Fig. 52 of Plate XV illustrates the flow of a current of cold water through still water at the same temperature, while fig. 53 illustrates the flow of a current of warm water through still water at a much lower temperature. The directions of flow in both cases have been indicated by arrows in the margin of the photographs. The precise character of the motion is explained clearly by the diagrams in fig. 17. In both cases the current is made to pass through a rectangular channel and enter into a wide vessel of cylindrical shape and filled with water and then to exit into a similar channel diagonally opposite. All corners joining the channels with the wide vessel are rounded off and made to have stream line shapes. The channel and the vessel in horizontal and vertical sections are shown in fig. 16. The current in the channel is generated by allowing water under a certain "head" to fall flatly on the portion AB and then pass through a pair of fine wire mesh. The effect of wire meshes is to smooth out the disturbance due to the fall and to give rise to a uniform stream line motion through the channel. This is easily tested by colour lines.

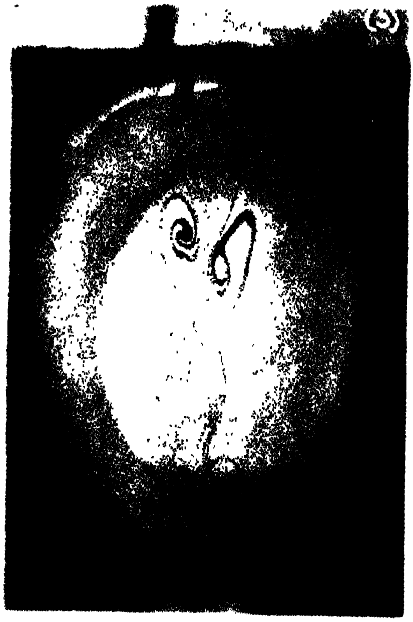


Fig. 52

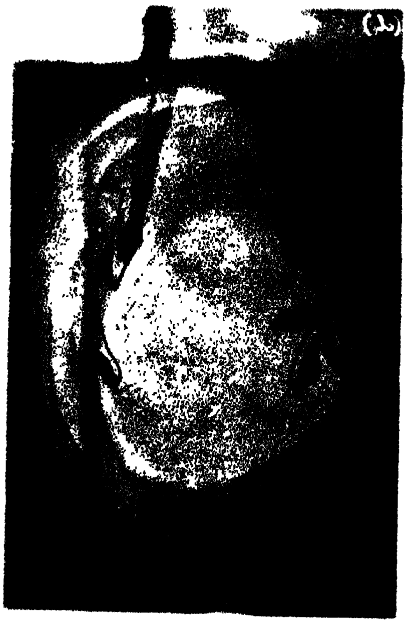


Fig. 53

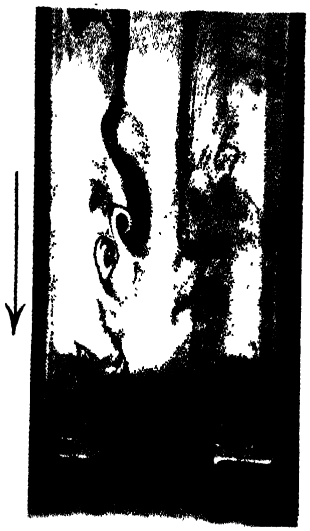


Fig. 54

0 2 4 cm
scale.

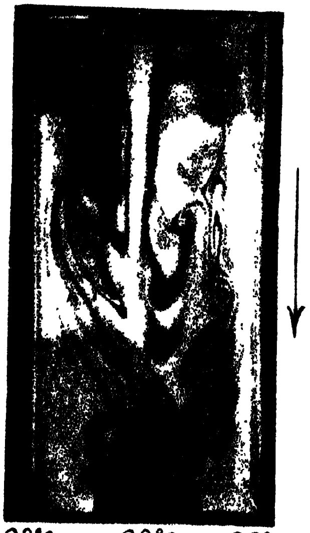


Fig. 55

Fig. 52. Showing the movement of a current of water through still water at same temperature.

Fig. 53. Showing the movement of a current of water through still water at lower temperature.

Figs. 54, 55. Showing the effect of sudden enlargement on a current of water.

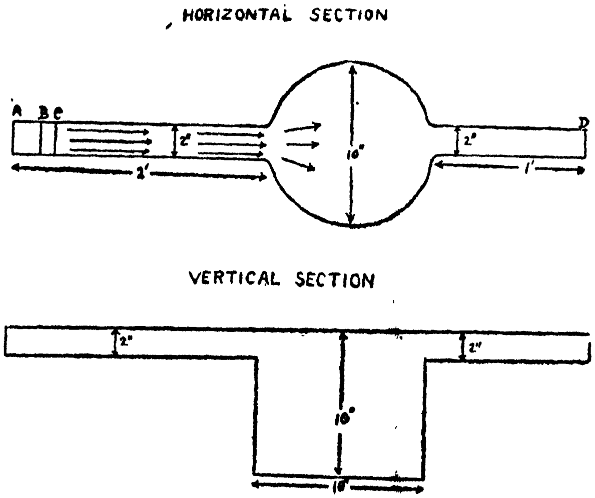


Fig. 16

It is seen from fig. 52 of Plate XV that the surface of discontinuity formed by a current of water flowing through still water at the same temperature tends to converge. Fig. 53 of Plate XV, on the other hand, shows that a current of warm water flowing through still water at a lower temperature will make the surface of discontinuity diverge. The convergence in the former case is purely the effect of the resistance offered by the still water to the current, while the divergence in the latter is due to the warm current ascending and spreading over the cold still water.

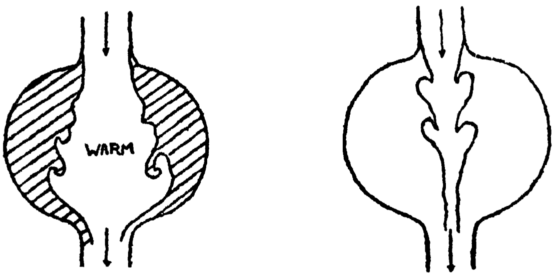


Fig. 17

It is important to realise that when the corners are rounded off, the well-known effect of a sudden enlargement on a current of water is to a great extent minimised. When a current is allowed to expand suddenly in a rectangular chamber in which the corners have not been rounded off the pattern obtained is shown diagrammatically in fig. 18. In fig. 54 and 55 of Plate XV have been given two photographs of the distribution of stream lines obtained under an arrangement of this kind. This is much more complicated than the type given in fig. 52 obtained under nearly the same temperature conditions. Nevertheless, even when the corners are rounded off this effect of expansion is present to a certain extent. In designing arrangements for introducing thermal discontinuites in moving liquids, it is important to eliminate this effect as far as possible.

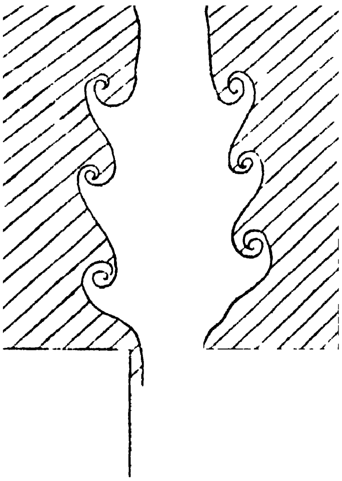


Fig 18

The arrangement used by Prandtl and others for the study of velocity discontinuities, with suitable modifications, appears to be the best for velocity as well as thermal discontinuities. This is shown diagrammatically in fig. 19. The main apparatus consists of a Y-shaped rectangular channel. The two side channels of section (5 in. × 6 in.) are about 3 ft. long and are made to meet at different angles in different apparatus. For most of the experiments the angle chosen was 10 degrees. The end of the wedge at O was carefully rounded off. The width of the joint channel is exactly double the width of the two side channels. Two streams, 'warm' and 'cold,' flowing through the side channels, meet each other at the joint channel. Under this arrangement the combined stream undergoes no expansion. CD and C′D′ are the two vertical glass windows and are used for taking photographs of the vertical section. The part CC′DD′ at the bottom is also fitted with a glass window for taking photographs of horizontal section. S is a perforated partition fixed at the open end of the joint tube. Different heights of this partition give different depths of water in the channel. The free ends of the side tubes are completely closed and a pair of fine wire gauge partitions (AB, A′B′) are used to give stream line flow in the channels. T_1 and T_2 are two thermometers and are used to record the temperatures of the fluids in the two channels. Y-shaped vessels of larger dimensions but of similar design were also used in order to vary the conditions of the experiments.

In order to get a steady flow, 'cold' as well as 'warm' water is brought in to the channels from two reservoirs under constant heads. The reservoirs used are very similar to Mariotte's bottles [fig. 19 (b)]. A large bottle, with an opening at the bottom, is fitted with a tight-fitting cork, through which pass two tubes, one short and the other long. The shorter tube is joined to the tap and the longer one is open to the atmosphere. When the water level in the bottle is above the lower end of the longer tube, the head of water which forces the water through the opening at the bottom is equivalent to XY [fig. 19 (b)], and is independent of the water level. Water from such a bottle was allowed to fall in the channel through a broad opening extending over the entire transverse section of the channel. The supply of warm water was obtained from a tank heated by means of gas stoves to the required temperature.

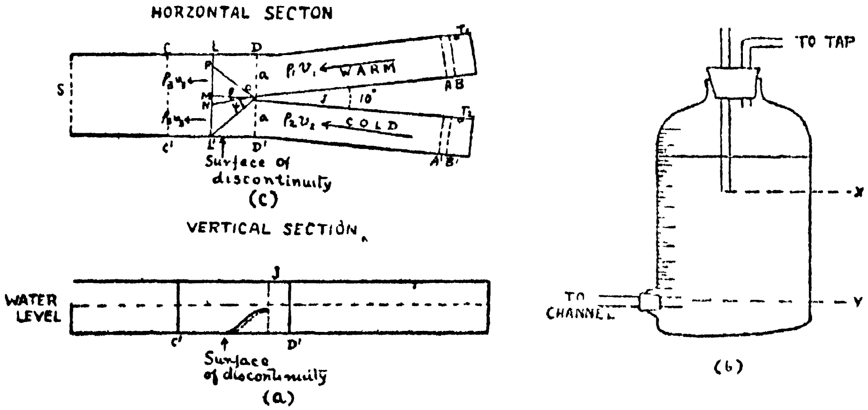


Fig 19

The quantities of water entering in the channels were regulated by means of screw-cocks and the flows tested to see if they gave straight stream-lines in the channels before photographs of the surface of discontinuity were taken.

The entire surface of the channels, except the glass windows, was painted white and the motion at the surface of discontinuity was traced by introducing colour in a suitable manner. Photographs of the horizontal section, were taken by means of a mirror, fixed above the apparatus, at an angle of 45° with the horizontal and exposing the camera to photograph the image in the mirror. Both sunlight and artificial light from powerful electric lamps were used for photographic purpose. The vertical section of the phenomena at the surface of discontinuity was photographed through the side glass windows. For this purpose one of the windows was covered with a thin white paper and illuminated by sunlight. In both the cases a scale was included in the field to be photographed to furnish the necessary reduction factor for the purpose of measurement.

Besides instantaneous photographs of horizontal and vertical sections, photographs were also taken of the paths of individual particles. For this purpose, the inside of the apparatus was painted black, and the liquid in the channel was illuminated through the side glass windows by means of sunlight coming through a narrow but long horizontal slit. A tiny white particle having the same specific gravity as that of water was dropped at a specific point of the surface of discontinuity. When the surface of water was viewed from above in a dark room, nothing could be seen except the particle which was rendered dazzling white by the sunlight and appeared as a bright point in the camera. To photograph the path of the particle, a time exposure was given.

The velocities of the currents in the two channels were measured by noting the time required for a light floating particle to traverse a certain known distance.

7. *General discussion of the phenomena observed at the surface of discontinuity between cold and warm currents.*

When two streams at different temperatures flowing in different channels meet each other, the surface along which they meet is not a vertical plane. It is a three-dimensional surface, and its shape depends on (1) the initial velocities of the two currents, (2) the angle between the two currents, (3) the temperature difference between the two currents, and (4) the time which has elapsed since the two currents met each other. The warm current being lighter ascends over the cold current and consequently the upper boundary of the surface of discontinuity is over the cold current; with the march of time when the surface of discontinuity has become diffused the warm current advances slowly towards the direction of the cold along the outer edge of the channel. On the other hand, the cold current being denser undercuts the warm current and consequently the lower boundary of the surface of discontinuity is below the warm current and remains almost stationary or advances very slowly towards the direction of warm current owing to the friction of the bed of the channel. Figs. 59 and 60 of Plate XVI show the upper and lower boundaries of the surface of discontinuity as viewed from above in relation to the wedge which separates the two currents. The disturbance is greatest in the upper boundary and least in the lower boundary. Fig. 56 of Plate XVI shows clearly that the motion at the upper boundary of the surface of discontinuity is precisely of the same type as we found in the case of plane discontinuity or cylindrical discontinuity in water which was initially at rest. As we move from the wedge in the direction of the current, we find a progressive growth in the vortices and this is accompanied by an increase in their dimensions. In the direction of the current there is an increase of amplitude as well as wave-length of the surface of discontinuity. The neat and almost perfectly symmetrical pattern as seen in this picture is attained only when the incident currents flow in stream lines with uniform velocity along the entire length of each channel. Non-uniform velocity in the incident currents or any disturbance in either or both of them is always associated with asymmetrical or diffused pattern of vortices at the surface of discontinuity.

In fig. 56 of Plate XVI, the temperature difference between cold and warm currents was only 10°C. When the temperature differnce is greater, the form of the vortices, viewed from above (horizontal section), is shown in the photographs figs. 57 and 58 of Plate XVI. It is seen that there is greater diffusion in figs. 57 and 58 than in fig. 56, but figs. 56, 57 and 58 are not strictly comparable for the exposures were not given in the three cases after the lapse of an equal interval of time since the two currents first met each other. The longer the time the two currents remain in contact with each other, the greater is the diffusion, inspite of the continuous renewal of

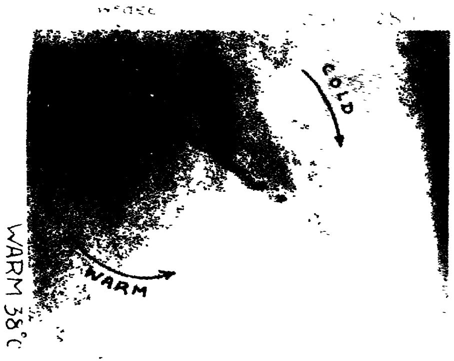


Fig 56

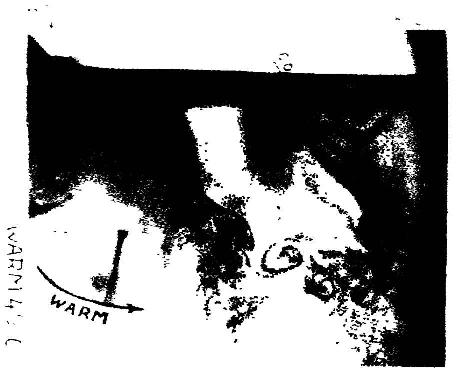


Fig 57

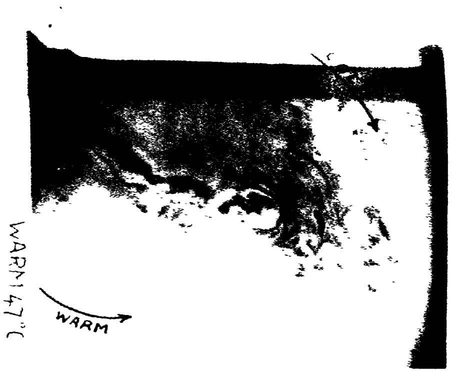
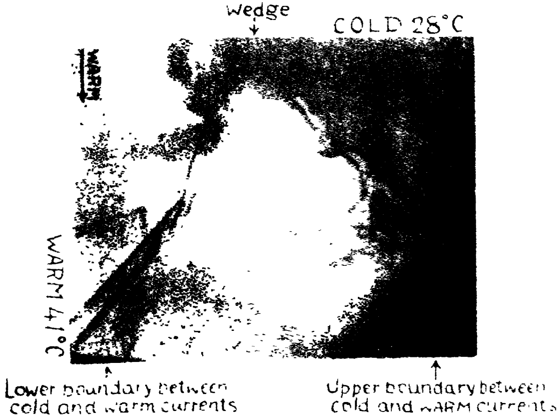


Fig. 58

Fig 59


wedge
COLD 28°C
WARM
WARM 41°C
Lower boundary between cold and warm currents
Upper boundary between cold and WARM currents

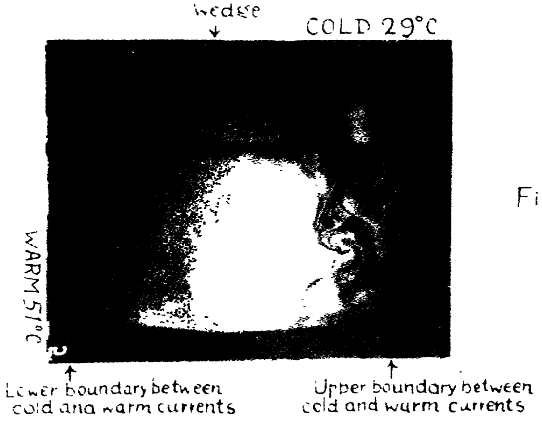

wedge
COLD 29°C
WARM 51°C
Lower boundary between cold and warm currents
Upper boundary between cold and warm currents

Fig 60

Figs. 56, 57, 58 Showing the form of surface of discontinuity between cold current (1·5 cm./sec.) and warm current (2·5 cm /sec.) meeting each other at an angle of 30 degrees (view from above).

Figs. 59, 60. Showing the upper (free surface) and lower (bottom) boundaries of surface of discontinuity,

the supply. The sharpness of the temperature contrast at the surface of discontinuity diminishes gradually and consequently the vortex pattern undergoes a change. This is clearly shown by the photographs in Plate XVII (figs. 61, 62, 63 and 64). These photographs were taken at 45 secs., 60 secs., 75 secs. and 90 secs., respectively, after the two streams met each other. They, therefore, show the growth and movement of the vortices with time as viewed from above. The initial temperatures of cold and warm currents were 25°C. and 41°C. respectively. It is seen from the successive photographs that with the advance of time, the vortices not only increased in dimensions but they became more and more diffused.

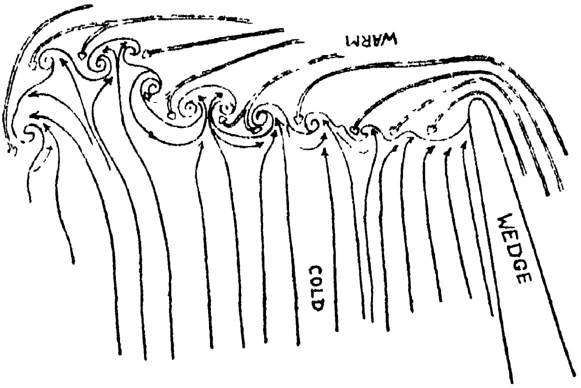


Fig 20

To understand completely the nature of the motion involved in the production of the vortices on the three-dimensional surface of discontinuity, it is necessary to analyse the motion both in the horizontal and vertical sections. An analysis of all the photographs of the horizonal section taken under different conditions suggests that the horizontal section of the vortex near the upper surface is of the type shown diagrammatically in fig. 20. Figs. 65 and 66 of Plate XVIII give two photographs of the stream lines on the discontinuous surface projected on the vertical plane. Owing to the difficulty of introducing colours in a vertical section, the filament lines are faint in the photographs. The drawing given below each photograph shows the nature of these lines. When the pictures of the horizontal and vertical sections are combined, the motion is of the kind as shown in perspective in Fig. 21.

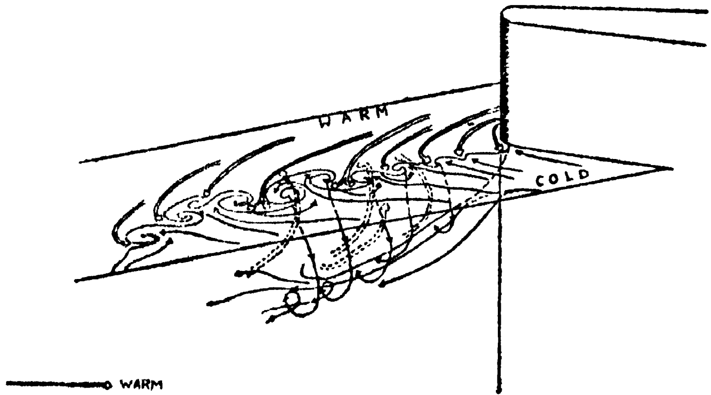


Fig. 21. (Perspective.)

It will be seen from the photographs that at the surface, near the wedge, the discontinuity has a wavy form. Further away each crest has developed into a spiral vortex, the growth being more and more as we move away from the wedge. As a rule the crests show greater development than the troughs. The direction of rotation of a vortex becomes opposite according as the supply to the core comes from the warm or the cold current or the turning moment is one way or the other according to the directions of the relative flows, which do not always maintain their original directions owing to the various disturbing influences which operate on the original currents. To picture the motion in three dimensions, one has to remember that the surface of discontinuity has a 'warm' side and a 'cold' side. At the warm side there is an upward motion overrunning the cold current, and at the cold side there is a downward motion under-cutting the warm current. While this is the general character of the motion at a little distance away on either side of the three-dimensional surface of discontinuity, the

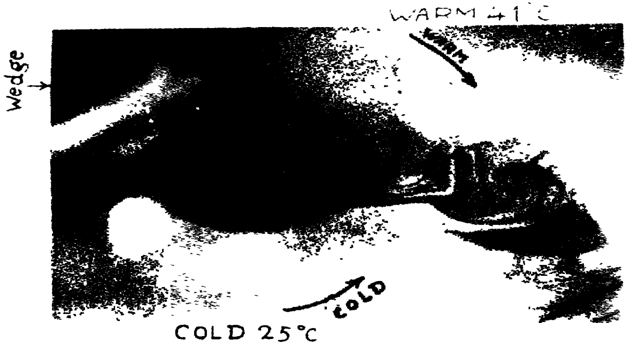


Fig. 61 (45 Sec)

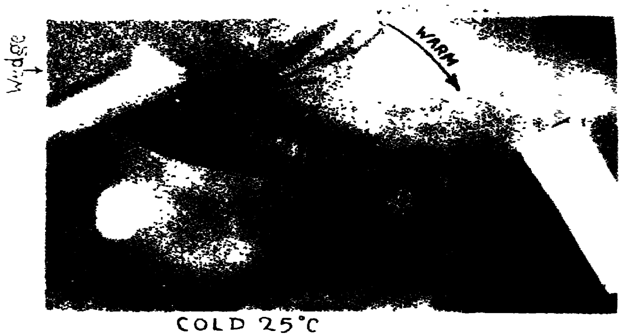


Fig. 62 (60 Sec)

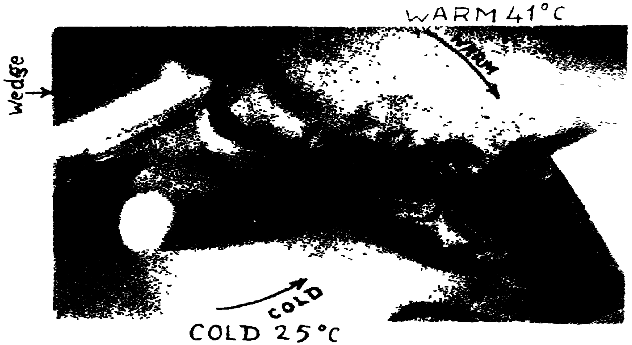


Fig. 63 (75 Sec.)

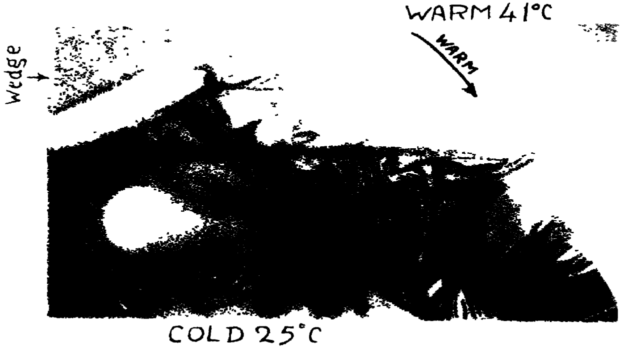


Fig. 64 (90 Sec.)

Showing the growth and movement of vortices with time (with view from above). The instants at which the photographs were taken after the two currents met each other have been shown against the figures. The cold and warm currents met each other at an angle of 10 degrees.

Cold current, 1·5 cm/sec., warm current, 2·5 cm/sec.

motion is more complex very close to the surface of discontinuity. At the core of a vortex the motion is minimum and the intermixing has apparently been greatest during the process of its formation. Consequently the temperature at the core is generally lower than that of the immediately surrounding water. Moreover, in a crest vortex the supply to the core comes from cold water. The core will therefore have a tendency to sink down and if it is over the warm side of the surface of discontinuity, the drop will be fairly rapid. The sinking down of the core is distinctly shown by the photographs 65 and 66 of Plate XVIII. The sinking does not occur vertically downwards but along an inclined line in the warm side almost parallel to the surface of discontinuity. The sinking of the core can be recognized by means of the faint lines proceeding from some of the cores towards the warm side in the horizontal picture 56 of Plate XVI and also in the pictures 57 and 58 of the same Plate. While sinking downwards, the line may be caught in the whirl and become a 'spiral' lower down the surface or undergo a complete turn and move in the direction of the general current. Complete evidence for the character of the motion as shown diagrammatically in fig. 21 can thus easily be found from the photographs given in Plates XVI and XVIII.

8. *The growth of vortices at the surface of discontinuity.*

The growth of vortices as we move from the wedge in the direction of the current can be seen from the numerical data given in Tables VII and VIII. It will be seen from the last two columns of Table VII that not only there is an increase in the diameter of the vortices in the direction of the currents but there is also an increase in the number of convolutions. Regarded as a double row of vortices, it is seen from Table VIII, that the quantity $\frac{\text{amplitude}}{\text{wave-length}}$ has very nearly the

TABLE VII.

Photo Number.	Temperature °C.			Distance from the wedge in cm. (actual).	Diameter of the first convolutions in cm. (actual).	No. of convolutions (2π × n) n.
	Cold.	Warm.	Diff.			
1	25·0	37·0	12	5·14	0·89	0·88
				7·00	1·04	1·00
2	25·0	42·0	17	5·43	0·30	1·00
				8·14	0·39	1·25
				10·42	0·53	1·31
3	25·0	43·0	18	4·14	0·24	1·15
				5·14	0·31	1·25
				6·00	0·37	1·75
4	26·0	45·0	19	5·54	0·18	1·25
				8·46	0·24	...
				12·00	0·33	1·50
5	25·0	45·0	20	4·16	0·15	1·37
				5·54	0·22	1·50
				6·16	0·35	1·50
				8·46	0·42	1·25
6	25·0	46·0	21	4·00	0·14	1·40
				5·43	0·24	1·57
				8·14	0·31	1·60
				11·71	0·37	2·00
7	26·0	48·0	22	4·29	0·12	1·75
				6·43	0·18	1·75
				8·29	0·27	2·00

Table VIII.

Photo Number.	Temperature. °C.			Vortex number counted in the direction of the current.	Distance between successive crest and trough vortices, (cm.).	Wave-length, cm.		Amplitude, cm.		$\frac{h}{\lambda}$
	Cold.	Warm.	Diff.			Observed.	Mean. λ	Observed.	Mean. h	
1	25·0	37·0	12	1						
				2	1·4	2·8	2·8	0·7	0·7	0·25
2	25·0	42·0	17	1						
				2	0·8	1·6		0·4		
				3	1·0	2·0		0·4		
				4	1·0	2·0	1·8	0·4	0·4	0·22
3	25·0	43·0	18	3						
				4	0·5	1·0		0·3		
				5	0·6	1·2		0·3		
				6	0·7	1·4		0·5		
				7	0·6	1·2		0·6		
				8	1·1	2·2	1·4	0·6	0·5	0·35
5	25·0	45·0	20	3						
				4	0·3	0·6		0·2		
				5	1·0	2·0		0·3		
				6	0·5	1·0		0·3		
				7	1·1	2·2		0·5		
				8	0·7	1·4	1·4	0·5	0·4	0·29
7	26·0	48·0	22	3						
				4	0·3	0·6		0·2		
				5	0·7	1·4		0·2		
				6	0·4	0·8		0·3		
				7	0·5	1·0		0·3		
				8	0·7	1·4	1·0	0·6	0·3	0·30

Mean ... 0·28

Kármán value. It is probably this fact which accounts for the stability of this type of vortices.

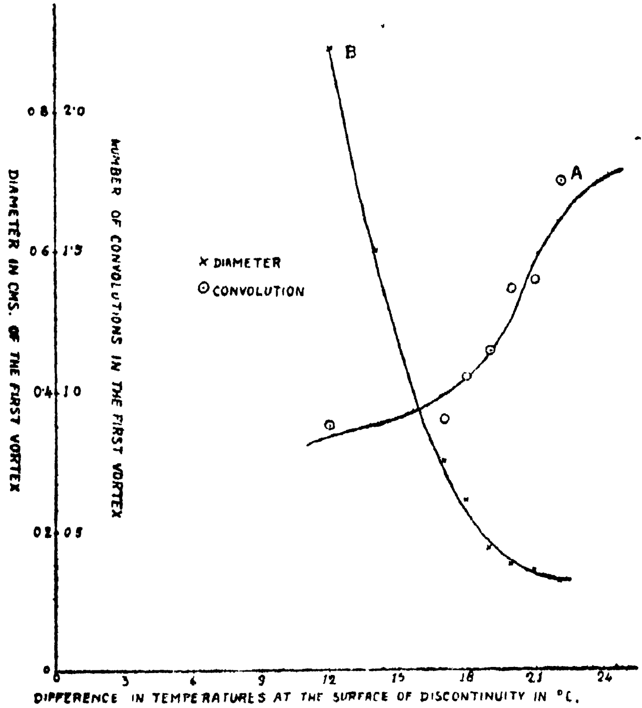
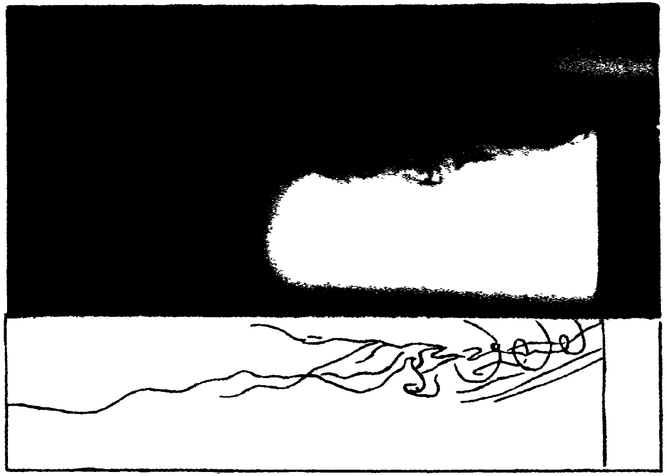


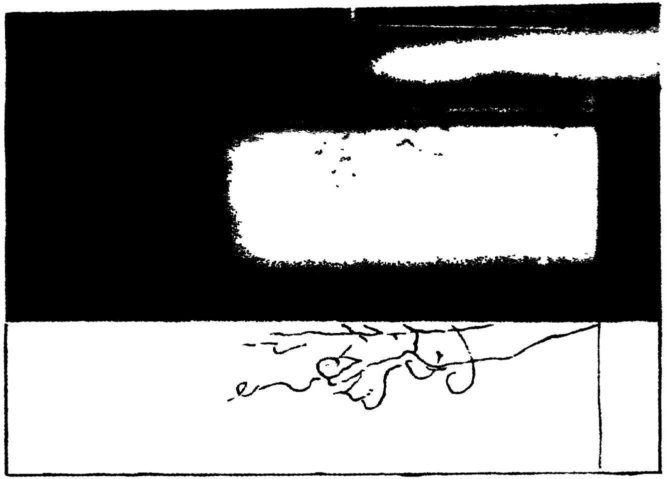
Fig 22

When the number of convolutions in the first vortex, nearest to the wedge, is plotted against the difference of temperature at the surface of discontinuity we get the curve A in fig. 22. From the trend of the curve, we can see that for temperature difference lower than 10°C, there is very slow increase in the number of convolutions with increase in the difference of temperature but for greater difference of temperature, the number of convolutions undergoes a rapid increase with increase in the difference.

In the same figure (fig. 22, curve B), the diameter of the first vortex has been plotted against the difference of temperature at the surface of discontinuity. It will be seen that the diameter increases rapidly with *decrease* in the difference of scale 0 2 4 cm.



Front: cold stream, temperature, 27 °c.
Rear: warm stream, temperature, 37 °c.
Fig. 65



Front: cold stream, temperature, 28 °c
Rear: warm stream, temperature, 38 °c
Fig. 66

Showing the filament lines on the discontinuous surface projected on a vertical plane.

Owing to the difficulty of introducing colours in vertical sections, the lines are faint in the photographs, the drawings given below each photograph show the nature of these lines.

temperature. The curve in fact becomes asymptotic to the diameter-axis. These results agree with those previously obtained for plane and cylindrical discontinuities in still water.

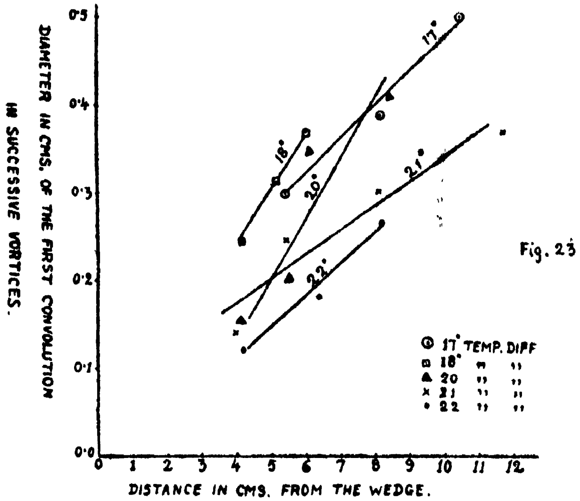


Fig. 23

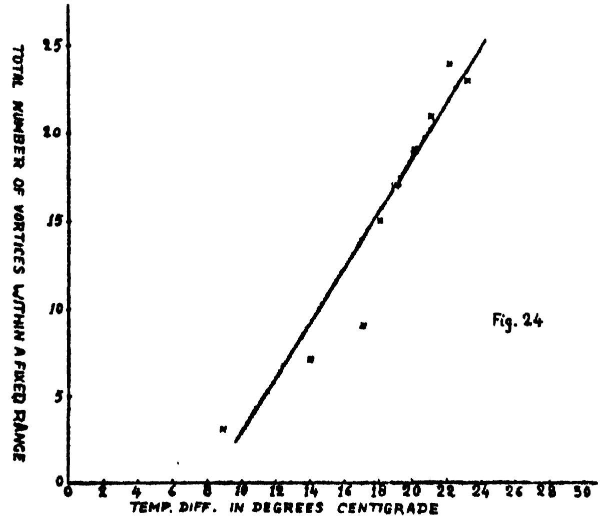


Fig. 24

In fig. 23, the diameters of the first convolution in the successive vortices have been plotted against their distances from the wedge for various differences of temperature at the surface of discontinuity. These curves clearly suggest that the diameters of the vortices in any row become greater the lower the difference of temperature at the surface of discontinuity. As a consequence of this law we would naturally expect that a larger number of vortices would appear on any photograph if the temperature difference at the surface of discontinuity is greater, provided the photograph includes the same range of the surface of discontinuity in the channel. Fig. 24, in which the total number of vortices appearing in any photograph has been plotted against the temperature difference at the surface of discontinuity, shows that this is so.

9. *The slope of the surface of discontinuity.*

The slope of the surface of discontinuity has an intimate relationship with the dimensions of the vortices. Figs. 67, 68, 69 and 70 of Plate XIX give the slope of the surface of discontinuity between cold and warm currents for various differences of temperatures. For obtaining these photographs, colour was introduced along the extreme end of the wedge in such a way that a trace was obtained of the lower boundary of the surface of discontinuity beginning from the wedge down to the bed of the channel. This lower boundary of the surface of discontinuity is one of minimum disturbance. Consequently the colour lines remain more or less stationary for an appreciable time. The photographs represent the sideway views, that is to say, the projection of the slope on a vertical plane. In these photographs the cold and warm streams meet each other at an angle of 10 degrees.

It is easily seen from figs. 67 to 70 of Plate XIX, that as the temperature difference at the surface of discontinuity increases, its inclination to the horizontal increases. In fig. 70, the temperature difference is greatest and the slope of the surface of discontinuity is greatest, while in fig. 67 the temperature difference is least and the slope is also least. The actual inclination of the lines in relation to the temperature difference is given in Table IX.

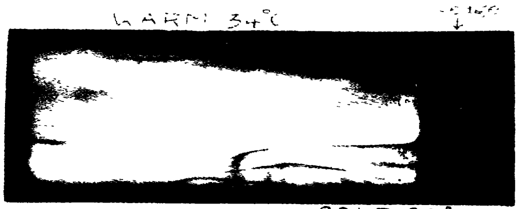


Fig. 67

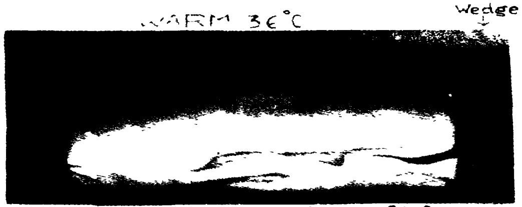


Fig. 68

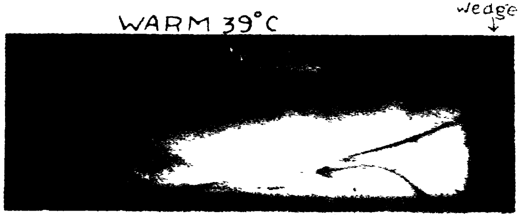


Fig. 69

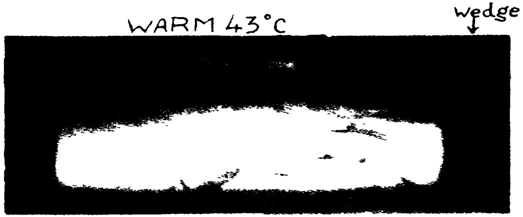
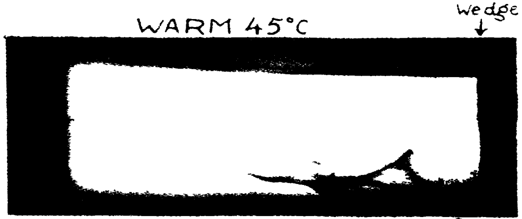
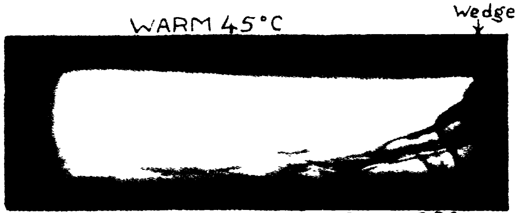


Fig. 70



After 1 min.

Fig. 71



After 3 min.

Fig. 72

Figs. 67–70. Showing the slope of the surface of discontinuity between cold and warm currents for various differences of temperatures. The photographs represent a vertical section through the wedge. The currents meet each other at an angle of 10 degrees.

Figs. 71, 72. Showing the change in the slope of the surface of discontinuity with time.

TABLE IX.

Photo number.	Difference of temperature in degrees Cent.	The angle made by the surface of discontinuity with the horizontal (degrees).
8	16	22
9	12	20
10	9	8
11	7	5

TABLE X.

Photo number.	Instant of exposure after the two streams met each other (sec.).	Initial temperature difference °C.	Angle made by the surface of discontinuity with the horizontal (degrees).
12	105	15	20
13	225	15	12
14	60	17	30
15	180	17	20

We have seen before that greater is the temperature difference at the surface of discontinuity, the smaller are the dimensions of the vortices. We thus obtain the result that greater the slope of the surface of discontinuity, the smaller are the dimensions of vortices. *The very small slope of the surface of discontinuity in the atmosphere and the small temperature difference undoubtedly account for the enormous dimensions of atmospheric cyclones.*

Obviously with increase in time, the temperature difference at the surface of discontinuity undergoes a diminution. We would therefore expect the surface of discontinuity to become more and more horizontal with increase in time. This is clearly shown by the photographs, figs. 71 and 72 of Plate XIX. The photograph in fig. 71 was obtained one minute and that in fig. 72 three minutes after the two streams met each other. The former shows greater slope than the latter. The actual change in the inclination of the surface of discontinuity with time has been given for two typical cases in Table X. We have already noted that with increase in time the vortices at the surface of discontinuity undergo an increase in dimensions and we can now associate this fact also with the decrease in slope.

10. *The change in the surface row of vortices and its direction with time.*

We have already pointed out that the surface row of vortices or the upper boundary of the surface of discontinuity lies over the cold current and makes a definite angle ψ with the common axis of the channel [see fig. 19 (*c*)]. This angle depends on the temperature difference between the cold and the warm currents and also their relative strengths. Since with the advance of time, the temperature difference at the surface of discontinuity undergoes a diminution, the angle ψ also undergoes a change. In the beginning it decreases rapidly and then becomes more or less steady. The changes in the row of vortices as well as in the angle ψ with the advance of time have been given in Table XI for one typical case.

TABLE XI.

Angle at wedge : 10°
Velocity of warm current : 2·5 cm./sec.
,, cold current : 1·5 cm./sec.
Cold stream : 25·0°C.
Warm stream : 41·0°C.

Photo number.	Instant of exposure after the two currents met each other in secs.	Distance from the wedge in cm. (actual).	Diameter of the vortices (actual) cm.	Number of convolutions (2π × n) n.	Total number of vortices which appear in the photo.	The angle between the surface row of vortices and the axis of the wedge.
19	45	7·0	1·7	0·50	4	55
		10·5	1·8	1·25		
20	60	4·8	1·5	1·00	8	48
		9·3	2·0	1·25		
21	75	3·8	1·3	1·25	12	48
		5·0	1·5	1·50		
		6·7	1·8	1·50		
		10·5	3·0			
22	90	3·8	1·5	1·75	13	45
		7·2	2·3	2·00		
		12·5	4·0	2·25		

It will be seen from the above table that with the advance of time, the diameters of the vortices in the row undergo generally an increase. The angle ψ which the row makes with the axis of the wedge is in the beginning 55°. It decreases to 48° after about 15 secs. and thereafter remains more or less steady at about 45 degrees.

If we measure the angle ψ which the row of vortices makes with the axis of the wedge for various temperature differences, we obtain the results given in Table XII.

TABLE XII.

Angle at wedge : 10°.
Velocity of warm current : 2·5 cm./sec.
Velocity of cold current : 1·5 ,,

Photograph number.	Difference of temperature in degrees Centigrade at the surface of discontinuity.	Number of vortices appearing in the photo.	The angle which the surface row of vortices makes with the axis of the wedge.
1	12	3	75
16	14	7	60
2	17	9	55
3	18	15	50
4	19	17	45
5	20	19	40
6	21	21	35
7	22	24	35
17	23	23	35
18	27	28	33

The table shows that with increase in the difference of temperature at the surface of discontinuity, the angle which the row of vortices makes with the axis of the wedge undergoes a diminution. It is seen from fig. 25 that the angle diminishes very rapidly for smaller temperature difference, but for higher temperature difference, the diminution occurs slowly. One would expect that greater the difference of temperature the more the warm current would extend over the cold and consequently the angle ψ should undergo an increase. One should also expect that with the lapse of time the warm current should spread more and more over the cold current and consequently the angle ψ should also increase. But the observations give quite contrary results. These facts are readily seen to agree with the variation of the slope of the surface of discontinuity with increase in temperature difference. We have seen that the warm current rises more abruptly upwards over the cold, the greater the temperature difference, thus giving a greater slope to the surface of discontinuity. If the slope becomes greater the angle ψ must necessarily become smaller.

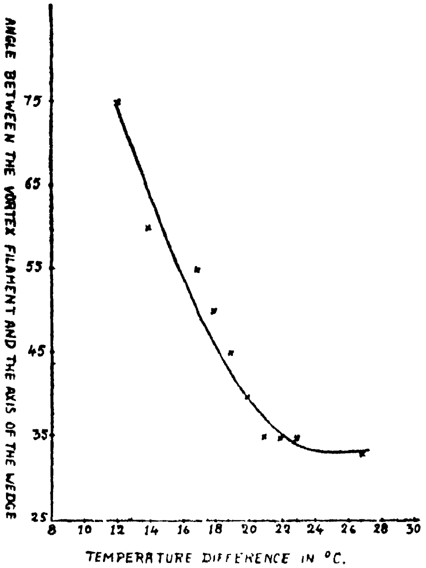


Fig 25

An explanation of the observed results can be easily obtained by an application of the equation of continuity in an approximate manner. Let us refer to fig. 19 (*c*). Let OL′ represent the upper boundary of the surface of discontinuity, that is to say, the direction of the surface row of vortices. Let OP represent the lower boundary of the surface of discontinuity.

If we draw a vertical plane ON so as to divide the "mass" of water included between the vertical planes through DD′ and LL′ equally, then we can consider approximately that the mass of water which enters through the vertical face OD passes through the vertical face NL and the mass of water which enters through the vertical face OD′ passes through the vertical face NL′. We can take the average density of water passing across the face NL to be approximately the same as the average density of water passing across the face NL′. We can assume that as a result of intermixing the velocity of water has approximately a uniform value across the face LL′.

Let us take

DO = D′O = a = breadth of 'cold' or 'warm' channel.

$$LN=c,\quad L'N=d,\quad OM=l,$$

$$\text{angle } MON=\theta.$$

Therefore

$$c+d=2a, \tag{1}$$

$$\tan\theta=\frac{a-d}{l}. \tag{2}$$

Let v_1 = velocity of the warm current,
v_2 = the velocity of the cold current,
h = depth of water,
ρ_1 = density of warm water passing across face DO,
ρ_2 = density of cold water passing across face D′O,
v_3 = common velocity of water passing through the face LL′,
ρ_3 = common density of water passing across the face LL′.

Now applying the equation of continuity to the volumes enclosed between the vertical planes DO, ON, NL, LD and between the vertical planes D′O, ON, NL′, L′D′, we get

$$\rho_1 ahv_1=\rho_3 chv_3, \qquad \ldots \quad (3)$$

$$\rho_2 ahv_2=\rho_3 dhv_3. \qquad \ldots \quad (4)$$

Therefore

$$\frac{\rho_1 v_1}{\rho_2 v_2}=\frac{c}{d}=\frac{2a-d}{d} \qquad \ldots \quad (5)$$

Let us suppose that v_1 and v_2 remain constant and the density of cold water also remains constant. If we increase the temperature of warm water, then ρ_1 will decrease. Consequently the ratio $\rho_1 v_1/\rho_2 v_2$ will decrease. We, therefore, see from (5) that the ratio $(2a-d)/d$ will become smaller. d therefore must become larger. We then get from (2), that θ must become smaller. It, therefore, follows that increasing the difference in temperature will make θ become smaller.

Let the surface row of vortices make an angle ψ with the axis of the wedge. In other words, let ψ be the angle L′OM.

Then

$$\tan \psi = \frac{a}{l}. \qquad \ldots \quad (6)$$

Using (2) we get

$$\tan \psi = \frac{a}{a-d} \tan \theta. \qquad \ldots \quad (7)$$

We have seen that increasing the temperature difference will cause an increase in the value of d and decrease in the value of θ. For both reasons therefore the right-hand side of (7) will become smaller. Increasing the temperature difference will therefore cause a decrease in the value of ψ. We thus obtain a qualitative explanation of the facts given in Table XII.

11. *Paths of particles at the surface of discontinuity.*

In order to elucidate further the nature of the motion at the surface of discontinuity, the paths of particles at the surface of discontinuity have been determined experimentally and these have been compared with those which would be obtained from theoretical consideration. For the experimental determination of the paths of the particles, the channels for cold and warm currents were painted deep black and placed in a dark room. A few tiny white particles composed of magnesium bicarbonate and spermaceti so as to have almost the same density as that of water were dropped at various points of the surface of discontinuity. Each of these particles appeared dazzling white when a horizontal beam of sunlight, entering into the room through a horizontal rectilinear slit, was allowed to pass through the glass windows of the experimental channels. As everything was painted black, nothing except the particles was visible. A photograph of the motion of the particles was obtained by the usual arrangement, that is, by having a mirror above the tank at an angle of 45 degrees with its surface and photographing the image. A time exposure was given so that as each particle moved over the surface of discontinuity, it traced a dazzling white line.

Figs. 73, 74, 75, 76, 77 and 78 of Plate XX represent some of the typical paths of particles. Fig. 73 represents the paths of the particles in the initial stage, that is to say, soon after the warm and the cold currents met each other. Figs. 74 to 77 represent the paths of the particles in the intermediate

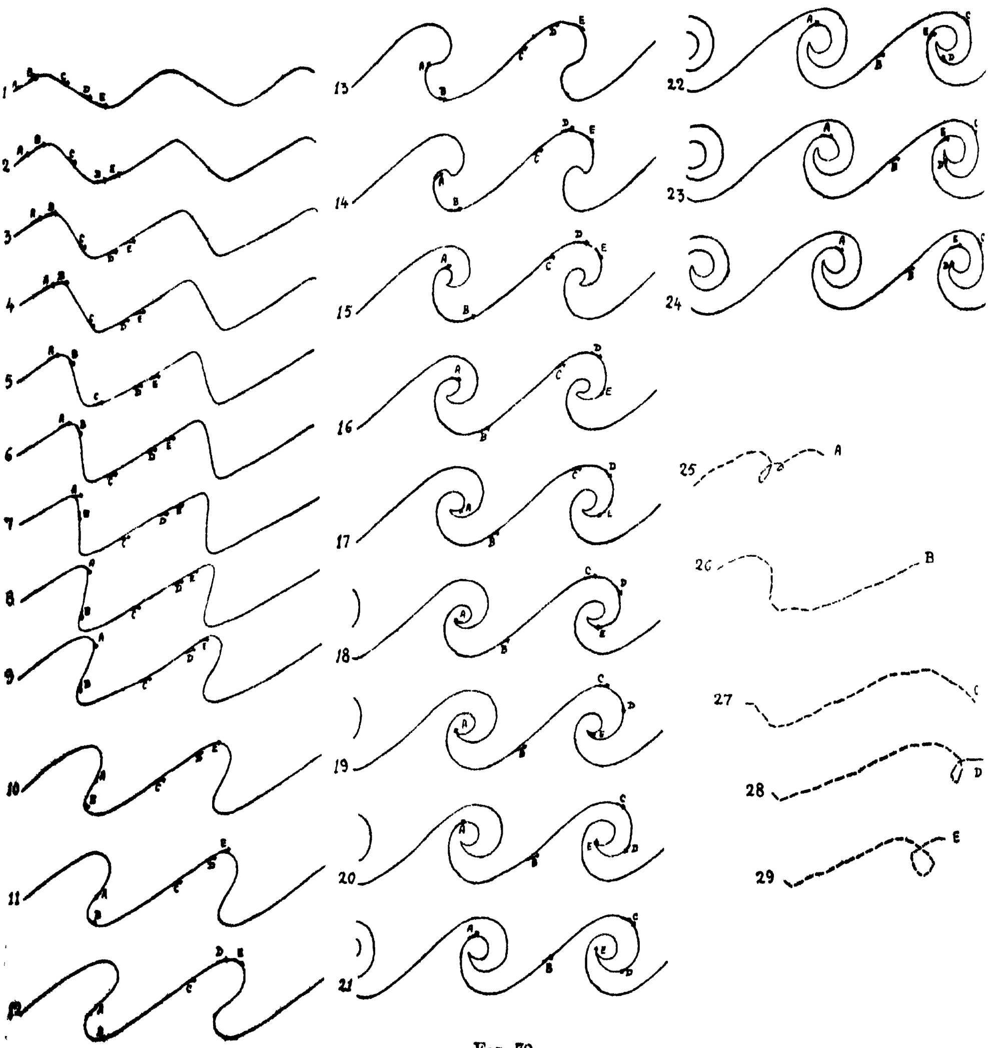


Fig. 79.

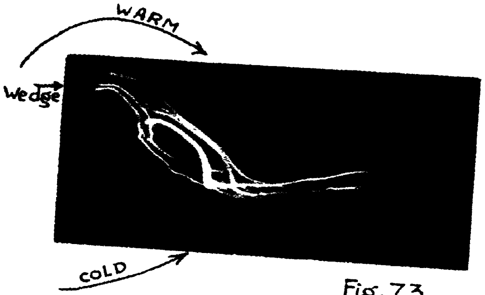


Fig. 73

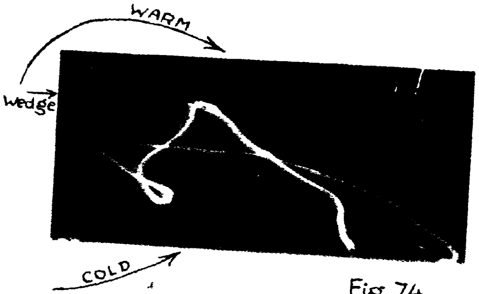


Fig. 74

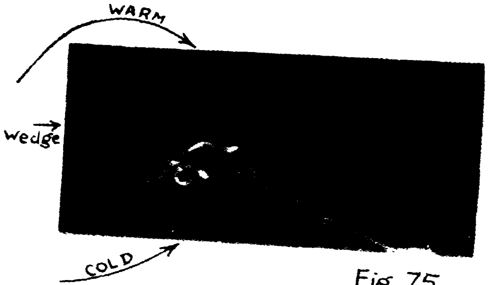


Fig. 75

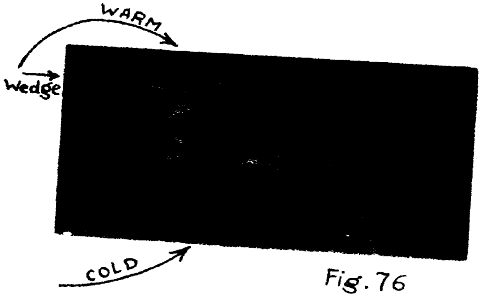


Fig. 76

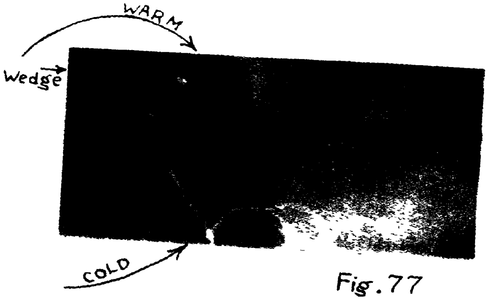


Fig. 77

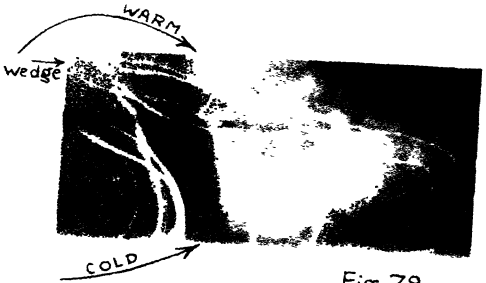


Fig. 78

Showing the paths of particles at the discontinuous boundary between warm and cold currents (view from above).

Fig. 73. Paths of particles in the initial stage

Fig. 74-77. Paths of particles during intermediate stages of development.

Fig. 78. Paths of particles at the final stage of dissolution.

stages of development of the vortices. Fig. 78 represents the paths of the particles at the final stage of dissolution ; that is to say, when the cold and warm currents have remained in contact with each other for such a long time that the surface of discontinuity has become very much diffused.

To trace the theoretical paths of the particles, the progressive growth and movement of the surface of discontinuity have been shown by a series of 24 curves (curves 1-24 of Fig. 79). These follow the law which holds in the case of an ideal discontinuity such as we would obtain by an application of the theory developed by Rosenhead. Each curve in the series shows a greater development of the surface of discontinuity than the preceding one and at the same time the surface of discontinuity is given a uniform translational motion. The starting positions of 5 particles (covering a complete wave) are indicated by the five arrows A, B, C, D, E in Curve 1. The positions of these arrows are then traced in the successive curves. In any particular position of an arrow, its length is determined by the resultant velocity due to the translational motion of the wave system and rotation round the pole of the vortex, both being supposed to be uniform. By joining together the different positions of the arrows in the successive curves we get the paths of the particles. These are shown by the curves 25, 26, 27, 28 and 29 of fig. 79. They will be found to have forms very similar to those given in Plate XX.

12. *Summary.*

The work of Prof. Prandtl and others shows that a surface of discontinuity in a fluid is unstable, that it changes into wave form and that the waves finally develop into three-dimensional vortices. The discontinuity may be one of motion, or of density, or both. While considerable work has been done under laboratory conditions regarding the phenomena involving discontinuity in motion only, very little work appears to have been done when there is discontinuity in temperature or both in motion and temperature. In the present paper an investigation has been made of the phenomena observed at, and in the neighbourhood of, a surface of discontinuity of the latter class. A discontinuity in density was introduced by making a cylindrical or a rectangular column of water in a large tank to have different temperature from the adjoining liquid, while a discontinuity in motion as well as density was introduced by making two streams of water under different thermal conditions meet each other at various angles. In both cases the surface of discontinuity resolves itself into interesting patterns of three-dimensional vortices. The mechanism of these vortices, the relationship of their dimensions, vorticity, etc., with the temperature difference at the surface of discontinuity and its slope, the depth of liquid as well as the velocities of the incident currents and other factors have been studied in the paper by photographing in horizontal and vertical sections the stream lines obtained by colouring various parts of the liquid and by other measurements. The paths of the particles at the surface of discontinuity have been photographed by a special method.

The instability makes each crest or a trough take up the form of a breaker and then roll round itself. A succession of spiral-shaped vortices is thus produced. In the direction of motion, the vortices show a progressive increase in dimensions and number of convolutions. The greater the difference of temperature at the surface of discontinuity, or the greater its slope, the smaller is the diameter of the vortices. For very small difference of temperature the vortices have enormous diameters. The greater the difference of temperature at the surface of discontinuity, the more rapidly the vortices develop. Qualitative explanation of most of the results has been given by simple hydrodynamical methods or by means of the theory recently developed by Rosenhead.

THE OBSERVATORY, BOMBAY.
March 23, 1932.

16

On the Measurement of the Absorption Coefficient of some Indian Materials.

BY

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RESEARCH FELLOW, University of Madras.

(Plate XXI.)

(Received for Publication, 29th March, 1931.)

Introduction.

In the course of the acoustic analysis of certain auditoria in Madras, a few materials were met with in those auditoria for which no acoustic data were available on account of their purely local origin. A few such materials were floor and door mats woven out of cocoanut fibre and also seat cushions stuffed with the same material. The sound absorption coefficients for these materials had to be determined before the reverberation for these auditoria could be worked out. The Stationary Wave method using a Tucker Hot-wire Microphone [1] was adopted for measurement with certain modifications as regards the nature of the experimental pipe as well as the source of sound. Incidentally the absorption coefficients of certain other Indian materials like sawdust and paddy-husk have also been determined to find out if cushions stuffed with these materials could be used as efficient sound absorbents.

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[1] E. P. Paris, Proc. Phy. Soc., Vol. 39, 1927.

Principle of the Method.

When sound of a constant pitch and intensity is produced at one end of a long cylindrical pipe, the other end of which is closed by a good reflecting surface, stationary waves are set up inside the pipe with points of maximum and minimum pressure variations separated by a distance of a quarter of a wave-length of the incident sound. If A be the amplitude of the incident wave, the amplitude of the reflected wave is also equal to A, and hence the amplitude in the stationary wave is equal to 2 A at the loops and zero at the nodes. If on the other hand, the surface closing the farther end of the pipe were sound-absorbing, the amplitude of the reflected sound is not A, but some fraction of it, and if B be this amplitude, then we get inside the pipe a type of imperfect stationary waves with a maximum amplitude of A+B at the loops, and a minimum amplitude of A − B at the nodes, the nodes and loops being separated by a quarter of a wave-length as before. Corresponding to the amplitudes A and B of the incident and reflected waves, the energy of the incident sound is proportional to A^2 and that of the reflected sound to B^2, and hence the ratio of energy of the sound absorbed to the incident energy $= \frac{A^2-B^2}{A^2}$ and this has been defined as the coefficient of absorption. To determine A and B, the ratio of the maximum to the minimum amplitude in the stationary wave system is measured by means of a microphone or a Rayleigh disc resonator. If this ratio is $\frac{a}{b}$, then $\frac{a}{b} = \frac{A+B}{A-B}$ and *a* the absorption coefficient

$$\frac{A^2-B^2}{A^2} = \frac{4ab}{(a+b)^2} = \frac{4}{2+\frac{a}{b}+\frac{b}{a}}$$

Previous Work by this Method.

A large number of determinations of absorption coefficient have been made by previous workers using this method of stationary waves with slight modifications in the nature of the experimental pipe, the source of sound, or the method adopted for comparing the intensities at the nodes and loops of the pseudo-stationary wave. J. Tuma[1] of Vienna has used an ordinary listening tube for comparing the sound intensities. Weishbach[2] used in his measurements a wooden experimental pipe and an electrically maintained tuning fork as the source of sound. The maxima and the minima of sound were measured by an electromagnetic microphone and a string galvanometer. Next come the experiments of Taylor.[3] His experimental pipe was also a wooden flue and the source of sound an organ-pipe. A Rayleigh disc instrument was used for measuring the sound intensity. Sound from inside the flue-pipe was led to the measuring instrument by means of an exploring tube. Eckhardt and Chrisler[4] have used a loud-speaker for the source of sound and a telephone for comparing the pressure amplitudes. They were able to measure the absorption coefficient for notes of frequencies of the order of 2000 and 3000 which have not been reached by the previous experimenters. Their experimental pipe was tuned to the frequency of the source in each case which has been considered unnecessary by Paris. Paris[5] has used a loud-speaker actuated by a valve oscillator as the source of sound and a tuned hot wire microphone for measurements. Davis and Evans[6] at the National Physical Laboratory have measured the absorption coefficient using a loud-speaker actuated by a valve oscillator as the source of sound and a moving coil loud-speaker movement for measuring the sound intensity.

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[1] Tuma, Wien. Ber., 111, 402 (1902).

[2] Weisbach, Annalen der Phys., 33, 763 (1910).

[3] Taylor H. O., Phys. Rev., 2, 270 (1913).

[4] Eckhardt and Chrisler, Bureau of Standards Sci. Papers, No. 526 (1926).

[5] Paris E. T., *loc. cit.*

Davis and Evans, Proc. Roy. Soc., London, 89 (1930).

The Author's Method.

In the method finally employed by the author, the essential differences from the practices of the previous workers are (1) the use of a long rectangular box mounted on insulating rubber corks in place of the usual cylindrical earthen-ware pipe, (2) the use of a valve-maintained tuning fork as the source of sound by which the question of the constancy of the pitch of the sound during a course of observations was solved easily, (3) the maintenance of the intensity of sound at a steady value by the use of a milliammeter in the amplifier circuit of the source. A tuned hot-wire microphone was used for measuring the sound intensity at the nodes and at the loops.

Experimental Details.

The Source of Sound.

The source of sound was a valve-maintained tuning fork, the out-put from the valve circuit being amplified by a Push-pull amplifier of amplification factor over 3000. The loud-speaker was an electromagnetic high resistance one with a moving diaphragm. The intensity of sound from the loud-speaker was controlled by means of the filament rheostat of the amplifier, so that in the position of a node the microphone indicated a resistance change of about 25 to 30 ohms. Throughout a set of observations this intensity of sound was maintained constant as indicated by the steady reading of a milliammeter in the plate circuit of the last valve of the amplifier.

The Experimental Box.

It is a long rectangular box of teak-wood (Plate XXI gives the set-up of the complete apparatus) 12 ft. in length and $1\frac{1}{2}$ ft. square section and mounted on rubber-corks to prevent the vibrations of the floor affecting the microphone mounted inside the box. The box is of sturdy construction with planks $1\frac{1}{2}''$ thick and ribbed in the four corners longitudinally with ribs $2''$ square section. The upper side of the box is provided with doors one near the end where the specimen is mounted, and another near the middle to enable the readings of the positions of the microphone to be taken on a mm. scale fixed along the length of the box. To enable the microphone to be moved along the box, the microphone was mounted on an ebonite block with sloping sides so that the block could slide easily between two wooden strips fixed parallel to each other. The sides of the strips were made smooth and graphited so that the microphone could slide without jerk. Movement of the microphone was effected from the open end of the box by means of an endless loop of thin book-binder's twine passing round pulleys (Fig. 1).

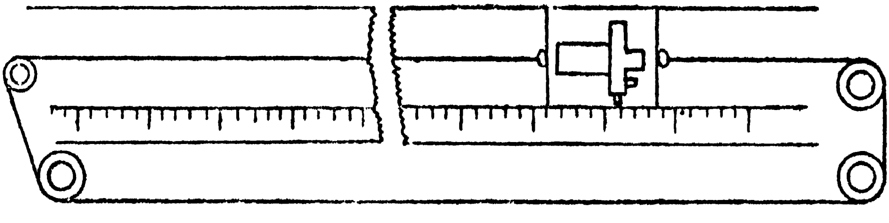

FIG. 1.

By this arrangement the microphone could be moved easily even by a millimetre at a time.

The end of the box to which the specimen was to be fixed was lined with a thick layer of felt and the absorbing specimens supported on teak-wood planks $1''$ thick were screwed on to the box.

The Microphone.

The microphone used was a tuned hot-wire microphone[8] the grid for which was obtained from Messrs. Sullivan & Co., London. The grid is a fine platinum wire bent into four loops and supported round a small glass-enamel rod fixed diametrically across the circular opening in a mica plate. The two terminals of the grid are soldered on to two silver foils one on either side of the mica plate. These two foils serve as electrodes for the grid. The grid was mounted in a cell provided with an adjustable resonator for tuning. The microphone cell was carried on an upright rod fixed to an ebonite block which slided in the groove along the length of the box.

Preliminary Experiments.

The suitable heating current for the microphone had to be determined by a preliminary experiment. The micro-

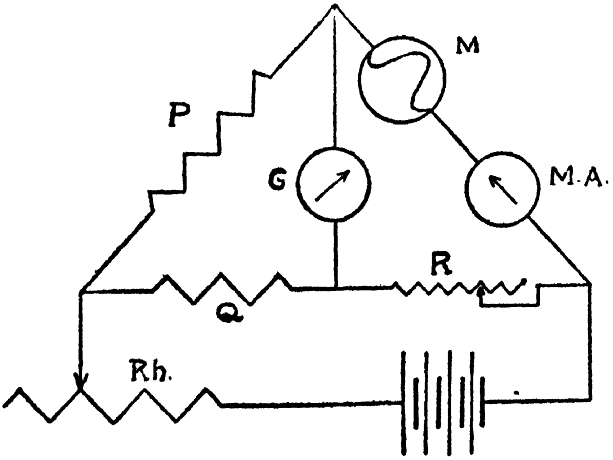

FIG. 2.

P & *Q*. Ratio arms of a P. O. Box.
R. The rheostat arm in series with a resistance wire for final adjustments.
Rh. A rheostat for controlling the current through the grid.
M. Microphone.
M.A. Milliammeter.
G. Micro-galvanometer.

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[8] A Selective Hot-Wire Microphone, Tucker & Paris, Phil. Trans. A, **221**, 389 (1921).

phone was arranged in a Wheatstone's circuit (Fig. 2) using a battery of sufficient voltage to give the desired heating current through the microphone. After securing the bridge-balance, when a sound of constant pitch and intensity was produced in front of the microphone, a deflection was produced in the micro-galvanometer in proportion to the change of resistance undergone by the microphone. The heating current was adjusted such that the deflection in the galvanometer was a maximum for a sound of constant intensity. This optimum working current was found to be about 30 milliamperes whereas the maximum safe current for the grid specified by the makers was 46 milliamperes. For currents more than 30 milliamperes the deflection was not only less but unsteady.

Next the resonator attached to the microphone cell was tuned to the pitch of the sound (frequency 384) intended to be used for the experiment. The same arrangement of apparatus as adopted in the previous case was used, and the resonator volume adjusted to give the maximum deflection in the galvanometer.

Before proceeding with the determination of the absorption coefficient, it was thought desirable to study the nature of the nodes and loops in the experimental pipe with a perfect reflector closing the farther end. For it has been pointed out by Davis and Evans [9] that the nodes and loops were well-defined only in pipes of circular section, and since the experimental pipe used by the author was of square section, the above investigation was thought necessary. The working microphone was fixed inside the box and the compensating microphone outside it with its mouth closed with a plug of cotton wool. The following electrical connections (Fig. 3) were adopted for measuring the change in resistance of the active microphone.

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[9] Davis and Evans, *loc. cit.*

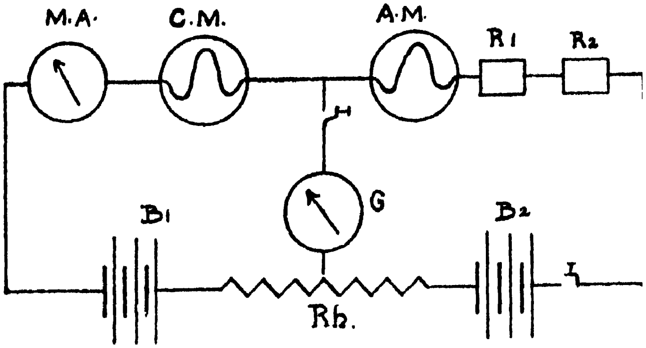
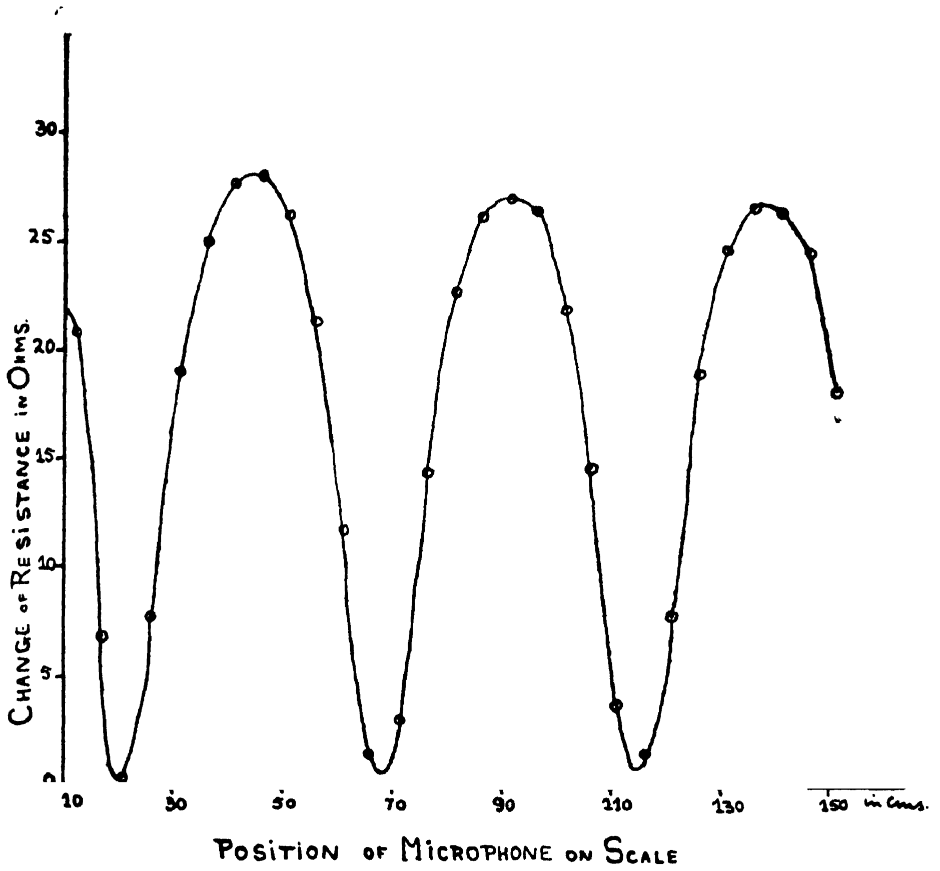


FIG. 3.

B_1 and B_2 batteries 6 volts each; Rh. rheostat 118 ohms ; C. M. compensating microphone ; A. M. active microphone ; M. A. milliammeter ; R_1 and R_2 resistance boxes including a decimal box ; G. a micro-galvanometer.

After making sure that the required current was passing through the microphones, balance in the sensitive galvanometer was secured by adjusting the position of the movable contact of the rheostat. The loud-speaker was next adjusted in front of the experimental box at a distance of a foot from its open end. The farther end of the box was closed by a brass plate $\frac{1}{4}''$ thick. When the loud-speaker was put on, the bridge-balance was disturbed as indicated by a deflection in the galvanometer, and this was restored by introducing suitable resistance on the active microphone side. Now the resistance introduced in the circuit gave the change of resistance undergone by the microphone grid which is a measure of the intensity of sound at the neck of the resonator. Thus beginning from very near the closed end of the box the intensity of sound was measured for every 5 cms. till about 3 or 4 nodes and loops were passed, the loud-speaker working throughout at constant strength. The values obtained when plotted in a graph given below, showed that the nodes were really not well-defined, but that the loops were very. sharp. In the actual experiment, since the important measurements are to be taken all near a loop region, and since in this region the microphone was sensitive to variations of its position even by a millimetre it was thought that the use of a pipe with a square section was not open to any objection.



Measurement of Absorption Coefficients.

Specimens Examined.

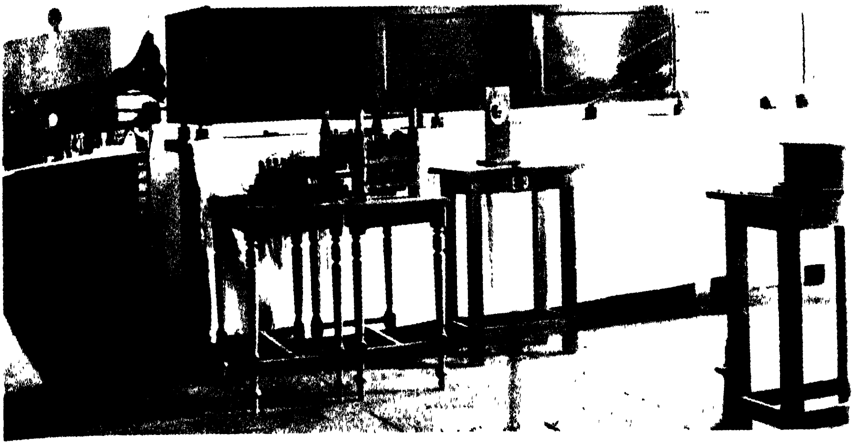
Coir mats of cocoanut fibre are manufactured on a large scale on the Malabar coast, and these are used ordinarily as door mats, and where it can be afforded, the whole of the floor is covered by suitable grades of such matting. The mat [Figs. (*a*) and (*b*) in Plate XXI] consists of closely packed bristles of the fibre, like a brush, held in the interstices of a coir matting of the same material, or sometimes of longitudinal strands of the material woven into particular patterns. These mats when dyed with different colours form suitable decorative coverings for the floor. Apart from their decorative aspect, their acoustic properties appealed to the author as worthy of measurement. Thus specimens of these mats were cut into square sections and mounted on suitable teak planks for backing them. These planks were screwed on to the experimental box during measurement.

Paddy husk and saw-dust were two other materials that were examined for their sound absorption when in bulk. Since these materials were obtained in plenty in this country, it was thought that bags filled with these stuffs might be used in auditoria for keeping down reverberation. Of course they cannot be used for seat cushions, since they are hard and get harder under pressure. A teak wood plank that could be screwed on to the box was provided with a ridge to a height of 1⅛″ into which this stuff was filled and covered over with a cloth and nailed. The plank thus fitted up was screwed on to the box.

Seat cushions stuffed with cocoanut fibre or cotton which are so common in all well-furnished auditoria were also examined for their sound absorption. They were stitched of specified dimensions to fit into the box and were backed by a teak wood plank as usual.

Experiment.

The same arrangement as was used for the study of the nodes and loops in the box was adopted. After the specimen was screwed on to the farther end of the box, the loud-speaker was actuated at the other end and the position of the microphone nearest to the specimen for a minimum resistance change was determined. Since in this position the resistance change was too small to be measured, and since its absolute



The set up of the apparatus.

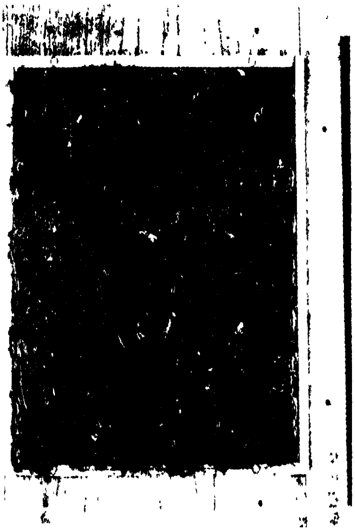


Fig. *(a)*

Fig. *(b)*

value was also not necessary, it was thought sufficient to observe the deflection δ produced in the micro-galvanometer included in the bridge arrangement. The microphone was next moved on to the position of maximum resistance change and this change of resistance R was determined by introducing resistances on the active microphone side to restore equilibrium of the bridge.

Now to convert these resistance changes into pressure amplitudes at the node and at the loop, the method adopted by Tuma and later by Paris was followed. A stationary wave was formed by replacing the absorbent specimen by the metal plate. The microphone was moved to the position of a node and the intensity of the sound of the loud-speaker was adjusted till the resistance change in the grid corresponded to R. Since in a perfect stationary wave the change of resistance at the node is more than at the node of a pseudo-stationary wave, the loud-speaker intensity had always to be diminished to make the change equal to R at the node of the perfect stationary wave. With this intensity of sound maintained constant, the microphone was moved on to a loop position and the displacement y of the microphone on either side of the loop required to produce a deflection δ in the galvanometer was determined. Now the ratio $\frac{a}{b}$ of the pressure-amplitudes at the node and at the loop of the pseudo-stationary wave $=\frac{1}{\text{Sin Ky}}$ where $K=\frac{2\pi}{\lambda}$ and a the absorption coefficient of the specimen

$$-\frac{}{2+\text{Cosec. Ky}+\text{Sin. Ky}}$$

The wave-length of the sound used in the above calculation was obtained by determining the position of two consecutive loops and multiplying the distance between them by 2.

Results.

Table I gives the tabulated value of the results obtained. The results given are the average of readings obtained on several occasions.

Discussion of Results.

The floor mats [Figs. (*a*) and (*b*) in Plate XXI] have coefficients of absorption ·2 and ·26 respectively. This is consistent with the difference in the making of the mats since the latter is of a denser variety and thus absorbs sound better. Used in large quantities where necessary for covering the entire floor they may be expected to add substantially to the total absorption in an auditorium.

Coloured designs are generally woven on such mats [Fig. (*b*)] which make them resemble decorative curtains, and such mats can be used for covering even wall spaces. Saw-dust and paddy husk exercise nearly the same amount of absorption, about 0·35. Bags filled with these materials can be usad as efficient sound absorbents if present in auditoria in some unobtrusive corners. The cushion filled with the cocoanut fibre has a higher coefficient of absorption than the one filled with cotton. This is due to the too close packing of the material in the cotton cushion. The cocoanut fibre does not allow of such close packing and as such gives a more porous and hence a better absorbing cushion. Use of such cushions in auditoria where additional absorption is necessary, will not only produce the desired effect, but add to their dignity and comfort.

TABLE I.

Specimen under test.	Specimen in position.			Reflecting Plate in position, microphone readings when ohmic change in grid was P_1.						Mean value of 2Y	Position of 1st loop $\frac{A+B}{2}$	Position of 2nd loop $\frac{C+D}{2}$		KY	
	Deflection of galvanometer for ohmic change P_1.		2 in chns.	Near 1st loop.			Near 2nd loop.								
	1st Min.	2nd Min.		A	B	2Y	C	D	2Y						
Door mat (*a*) ...	1	1	19	21·9cm	20·2	1·7	69·2	67·5	1·7	1·7	21·05	68·35	47·3	3°·14′	·2021
Door mat (*b*) ...	1·5	2	18·3	22·2	19·9	2·3	69·8	67·4	2·4	2·35	21·05	68·6	47·55	4°·27′	·2674
Saw dust ...	6·5	7·0	20·0	22·4	19·3	3·1	69·7	66·5	3·2	3·15	20·85	68·1	47·25	5°·59′	·3416
Paddy husk ...	6·0	6·0	20·6	22·55	19·20	3·35	69·75	66·5	3·25	3·30	20·92	68·12	47·2	6°·18′	·3497
Cotton cushion ...	7	6·5	19·6	22·95	18·4	4·55	70·2	65·5	4·7	4·63	20·68	67·85	47·17	8°·50′	·4617
Coir cushion	8	9·0	18·6	23·5	18·3	5·20	70·9	65·6	5·3	5·25	20·90	68·25	47·35	10°	·5041

17

Are Argon and Methane Molecules Optically Anisotropic ?

By

S. PARTHASARATHY.

(*Received for publication, 4th May, 1932.*)

ABSTRACT.

With a high-speed camera specially constructed for this work, the transversely scattered radiations from the gases argon and methane, excited by light polarised with electric vector parallel to the direction of observation were examined for polarisation with a quartz double-image prism. In each case, the scattered light was found to be unpolarised, thus establishing definitely that these molecules oscillate as anisotropic electric dipoles in the field of the light wave. If the atom radiates also as a magnetic dipole or an electric quadrupole, the contribution from it to the observed scattering is too small to be observed. An explanation is advanced tentatively, that this observed optical anisotropy might arise from atoms and molecules temporarily springing up into the excited state; the normal and the excited states being different optically.

1. *Introduction.*

The normal state of the argon atom is expressed in the spectroscopic language by the term $^1S_0$ and a closed shell of eight electrons. It is therefore chemically inert, forming no compound. Observations on the dielectric constant of the gas have been made by V. Braünmuhl[1] who finds no electric moment for its atoms. Argon crystals (m. p. −189°C) have been shown by Wahl[2] to be isotropic and to belong to the cubic system. X-ray analysis[3] of solid argon also shows it to be a face-centred cubic lattice, with the closest spherical packing. These observations suggest a spherical form for the argon atom. It is surprising, therefore, to find that light scattered transversely by the argon gas shows a depolarisation of 0·56%.[4]

The case of methane gas is equally surprising. It exhibits a depolarisation of 1·14%[4,5] in light-scattering which does not seem easy to reconcile with the tetrahedral form suggested by chemical considerations and by the X-ray analysis of solid methane by the powder method by McLennan and Plummer[6] who confirm the existence of the cubic form, in which the molecules are in a face-centred lattice. The tetrahedral form is supported by the observation of Sanger[7] who finds that the molecule has no electric moment. Wahl[2] found that the growth-structures of methane (m. p. −184°C) were developed according to the hexahedron. The crystals are isotropic, with the four trigonal axes of symmetry characteristic of the cubic system. It should be mentioned, however, that Wahl[8] has reported also the existence of a doubly refracting enantiotropic form of methane at very low temperatures. Evidently, methane is polymorphous, like all other compounds of carbon of the type CX_4. Moreover, McLennan and Plummer do not exclude the possibility of pyramidal form for methane, from their

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[1] Phys. Zeit., 28, 141 (1927).

[2] Proc. Roy. Soc., 87, 371, (1912).

[3] Simon and V. Simson, Zeit. Physik, 25, 160 (1924).

[4] Rayleigh Proc. Roy. Soc., Vols. 97 and 98, pp. 435 and 57 (1920) Cabannes, Ann. Phys., 15, 5 (1921) and the author in Ind. Jour. Phys., Vol. 7, 139 (1932).

[5] Cabannes and Granier, Comp. Rend., 182, 885 (1926).

[6] Phil. Mag., 7, 761 (1929).

[7] Phys. Zeit., 27, 556 (1926).

[8] Proc. Roy. Soc., 90, 18 (1914).

X-ray analysis, apparently confining themselves to the existence or otherwise of the cubic form.

The explanation generally offered for the depolarisation of light scattering by molecules is that they behave in the field of the light-wave as anisotropic electric dipole radiators. This is the most natural explanation in view of the fact that the size of molecules is very small compared with the wave-length and it is supported by a large body of evidence, especially by the relation which has been established between depolarisation and birefringence, natural or artificial. There is, however, an additional possibility, namely, that the molecules radiate also as electric quadrupoles or as magnetic dipoles in which cases, incident natural light scattered transversely would exhibit partial depolarisation even if the molecules were isotropic. This is clearly illustrated by the theoretical treatment given by J. J. Thomson of the scattering of light by perfectly conducting spherical particle of small size, and by the investigations of Mie[9] on the scattering of light by large spherical dielectric or imperfectly conducting particles. It is known to spectroscopists that quadrupole radiation from atoms may occur, and it is, therefore, of interest to consider the possibility of similar types of radiation appearing in molecularly scattered light and being responsible for its partial depolarisation.

A simple method of distinguishing the electric dipole radiation from the magnetic dipole or electric quadrupole radiation is by examining the light scattered transversely by atoms and molecules excited with plane polarised light, with the electric vector parallel to the direction of observation. Such scattered light with the anisotropic electric dipole is unpolarised, while in the other two cases, it is polarised, but with vibrations perpendicular to the direction of observation.

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[9] Ann. d. Phys., 25, 377 (1908). See also Sir C. V. Raman, 'Nature,' 128, 795 (1931).

It was thought worthwhile to examine the cases of argon and methane in this manner.

2. *Experimental.*

The general experimental arrangement is the one usually followed in all scattering experiments, with some modifications, such as for polarising the incident light for this work.

The bright tungsten bead of a 500 c.p. pointolite lamp was used as the source of light. An image of it was focussed by a system of lenses about 1·3″ from the source into the gas contained in a cross-tube similar to the one employed in previous investigations. Prior to entry into the gas, the light was polarised by means of a suitably oriented nicol, with the electric vector exactly parallel to the direction of observation. The state of polarisation of the transversely scattered light was recorded on a photographic plate using a specially devised high-speed camera with a Zeiss lens of focal length 3 cms. and an aperture of F/1 serving as the lens. A clear quartz double-image prism with the images exactly one above the other and at a distance quite sufficient to separate the two images was placed between the cross-tube and the camera.

The method adopted for getting a good focal plane for the photographic plate was the following. With the above arrangement and carbon dioxide in the cross tube, a series of photographs were taken with the double-image prism in front of the camera, for different positions of the camera lens. The lens was then fixed at the reading, giving the best focus for the two images of the track.

Very exact orientation of the nicol is perhaps the most important of all adjustments, considering the low depolarisation value for argon. Using a double-image prism, which gives the two images exactly one above the other, in front of the nicol, the latter could be set with the electric vector parallel to the plane of incidence and also of observation with an error of only half a degree. This position was also confirmed in the following way. With carbon dioxide in the cross-tube and the nicol at about the right position and at intervals of two degrees on either side of it, the transversely scattered light was photographed with the quartz double-image prism in the track of the scattered light. For the position of the nicol, where the electric vector is parallel to the plane of incidence, the two images should be of equal intensity. This was found to be so at reading 92°, agreeing with the first visual method. The above was repeated with oxygen and the position confirmed.

The cross-tube was thoroughly cleansed of organic vapours by heating it, since the latter generally give rise to the formation of clouds, a serious source of error in such experiments. The gases experimented upon were also rendered dust-free by passing them through tubes tightly packed with cotton wool.

With the above arrangement, the two polarised images scattered by CO_2 with incident horizontally polarised light, could be registered on the plate in an hour. Methane took about 10 hours and argon 48. Both the images were quite distinctly separate and well-focussed in each case.

Ilford golden Iso-zenith plates of H and D 1400 backed with caramel solution were used in the investigation.

3. *Results.*

With the incident plane polarised light as above, the scattering in argon, methane, oxygen and carbon dioxide was studied. In the case of argon, the scattering was observed at 86°, 90°, 92° (horizontal) and 94° readings of the nicol placed in the incident track. The two images at 92° were equal, showing that the scattered light was quite unpolarised; at 90° and 94°, it was very nearly so, but at 86° only the image of the track with vibrations perpendicular to the direction of observation was present.

In the case of the other molecules also, the scattered light was unpolarised. The two images of the track as got on the photographic plates were of equal intensity.

4. *Discussion.*

Examining now, the results for argon and methane, in the light of the foregoing discussion, we find that the imperfect polarisation in these two cases cannot arise from either a magnetic dipole or an electric quadrupole. It seems to be fairly certain that argon and methane are genuinely optically anisotropic. Most probably, other spherical atoms and tetrahedral molecules are also so.

However, if they radiate also as in the other two cases, the scattering is too small to be observed.

Even though no definite experimental evidence is forthcoming for the cause of this observed optical anisotropy in argon, yet it may not be far wrong to put forward the suggestion tentatively, that atoms, themselves spherical normally, become anisotropic when excited; more so, under the field of the incident light wave, so that the moments A, B and C induced in the atom are different along its three principal axes.

The above can find an easy explanation in wave-mechanics. The argon atom in the non-excited state is expressed by an S term, which represents it as a symmetrical atom. On excitation, the transition is not to any other S state, which is forbidden, but to a 2P, 3P, etc., states, in which the charge distribution is not symmetrical. If the ground term is represented by the wave-function ψ and the excited state by ψ', then the probability of transition from the first to the second state is proportional to

$$\int x \psi \psi' \, d\tau$$

and the electric moment, being a vector, is given for the normal state, by $X_1 = Y_1 = Z_1 = \int x_1 \psi \bar{\psi} \, d\tau$

the distribution of charge being symmetrical, while for the excited,

$$X_2 = \int x_2 \psi' \bar{\psi}' \, d\tau$$

$$Y_2 = \int y_2 \psi' \bar{\psi}' \, d\tau$$

$$Z_2 = \int z_2 \psi' \bar{\psi}' \, d\tau$$

where $\bar{\psi}$ and $\bar{\psi}'$ are the conjugate functions of ψ and ψ'. It is clear from the above argument that the electric moments A, B and C for the excited atom cannot be equal. Argon, therefore, behaves as an anisotropic atom, the observed optical anisotropy being the result of the atom springing up into an unsymmetrical excited state, the transition to which is governed, by the product of the wave-functions for the two states.

The author desires to thank Prof. Sir C. V. Raman for his help and interest in the work.

18

A Generalised Formula in the New Statistics

By

M. K. GOPALAIENGAR.

(*Received for Publication, 4th May, 1932.*)

ABSTRACT

A generalised formula is derived on the basis of the new statistics, containing the solution of all the equilibrium problems. Simple substitutions in the formula are shown to lead to the well-known expressions for the pressure exerted by electrons, for the constant of chemical equilibria, for the vapour pressure of a crystal, etc., in the new as well as in the old statistics.

Consider an assembly of two or more closely related systems in equilibrium, contained within an adiabatic enclosure. According to the Pauli-Fermi Statistics the entropy of a system is given by

$$S=nk\left[\frac{5}{2}\frac{U_{\frac{3}{2}}}{U_{\frac{1}{2}}}-\log A\right] \qquad \ldots \qquad \ldots \qquad (1)$$

where $U_{\frac{3}{2}}$ and $U_{\frac{1}{2}}$ are particular cases of the general Sommerfeld integral

$$U_p=\frac{1}{\Gamma(P+1)}\int_0^\infty \frac{u^p du}{\frac{1}{A}e^u+1} \qquad \ldots \qquad \ldots \qquad (2)$$

In the case of interest, the entropy of the assembly as a whole is

$$S=\Sigma nk\left[\frac{5}{2}\frac{U_{\frac{3}{2}}}{U_{\frac{1}{2}}}-\log A\right] \qquad \ldots \qquad \ldots \qquad (3)$$

where the summation is to be taken over all the systems under consideration. If δn represents an arbitrary change in the number of individuals constituting one of the systems, there will be corresponding changes in the number in the other systems. The consequent change in the entropy δS is given by

$$\delta S = \sum \frac{\partial}{\partial n}\left[nk \left\{ \frac{5}{2} \frac{U_{\frac{3}{2}}}{U_{\frac{1}{2}}} - \log A \right\} \right] \delta n$$

Following a procedure exactly similar to that adopted by S. Chandrasekhar[1] and substituting, "if Q be the heat absorbed during the process" for the words "if Q be the heat absorbed during ionization" we obtain

$$\sum K\left[\frac{5}{2} \frac{U_{\frac{3}{2}}}{U_{\frac{1}{2}}} - \log A \right] + \sum \frac{nk}{A} \left[\tfrac{3}{2} - \tfrac{5}{2} \frac{U_{\frac{3}{2}} \cdot U_{-\frac{1}{2}}}{U^2_{\frac{1}{2}}} \right]$$

$$= -\frac{\chi}{T} + \frac{3}{2} \sum VK\beta \frac{1}{A} \frac{\partial A}{\partial n} \qquad \ldots \qquad \ldots \qquad (4)$$

This is the general formula that we referred to in our initial remarks. In solving any particular equilibrium problem, we must only substitute for U_ρ and A for each of the systems involved in the problem, the correct expressions according as it is degenerate or non-degenerate and sum up as indicated in (4).

If any of the systems of interest be non-degenerate then they conform to the laws of classical statistics so that

$$U_p = U_{p-1} = \quad \ldots \quad \ldots \quad = U_{\frac{3}{2}} = U_{\frac{1}{2}} = U_{-\frac{1}{2}} = A$$

and $$A = \frac{nh^3}{VG} (2\pi mkT)^{\frac{3}{2}} = \frac{n}{V\beta}.$$

Thus for this case

$$K\left[\frac{5}{2} \frac{U_{\frac{3}{2}}}{U_{\frac{1}{2}}} - \log A \right] + \frac{nk}{A} \left[\frac{3}{2} - \frac{5}{2} \frac{U_{\frac{3}{2}} U_{-\frac{1}{2}}}{U^2_{\frac{1}{2}}} \right] \frac{\partial A}{\partial n} - \frac{3}{2} VK\beta \frac{1}{A} \frac{\partial A}{\partial n} U_{\frac{1}{2}}$$

$$\ldots \qquad \ldots \qquad \ldots \qquad (5)$$

becomes simplified to $-k \log \frac{n}{V\beta}$, $\ldots \qquad \ldots \qquad \ldots \qquad (6)$

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[1] S. Chandrasekhar, Phil. Mag., Vol. 9, p. 272 (1930).

If any of the systems be degenerate, they obey the laws of the new statistics of Fermi and Dirac so that

$$U_p = \frac{u_0^{p+1}}{\Gamma(p+2)}\left[1+2\left\{\frac{p(p+1)c_2}{u_0^2} + \frac{(p+1)\,p.\,(p-1)(p-2)}{u_0^4}c_4 + \dots\right\}\right]$$

$$u_0 = \log A = \frac{h^2}{2mkT}\left(\frac{3n}{4\pi G}\right)^{\frac{2}{3}}$$

and $c_\nu = 1 - \frac{1}{2^\nu} + \frac{1}{3^\nu} - \frac{1}{4^\nu} + \dots \dots$ and in the special case when $\nu = 2$, $c_2 = \frac{\pi^2}{12}$.

Thus we approximately get

$$U_{\frac{3}{2}} = \frac{8u_0^{\frac{5}{2}}}{15\sqrt{\pi}}\left(1 + \frac{5}{8}\frac{\pi^2}{u_0^2}\right)$$

and

$$U_{\frac{1}{2}} = \frac{4u_0^{\frac{3}{2}}}{3\sqrt{\pi}}\left(1 + \frac{\pi^2}{8u_0^2}\right)$$

$$U_{-\frac{1}{2}} = \frac{2u_0^{\frac{1}{2}}}{\sqrt{\pi}}\left(1 - \frac{\pi^2}{24u_0^2}\right)$$

Thus (5) reduces on simplification to the form (V being unity)

$$\left(\frac{3n}{4\pi G}\right)^{\frac{2}{3}} + \frac{\pi^2 K^2 mT}{12h^2}\left(\frac{4\pi G}{3n}\right)^{\frac{2}{3}} \qquad (7)$$

Applications :—

(1) Electrons in equilibrium with metal.

This problem involves two systems, *viz.*, the electrons outside the metal and those within it, with the aid of formulae (4), (6) and (7) we can calculate the pressure exerted by the electron gas, considering any of them to be degenerate or non-degenerate, when both the outside (*nf*) and inside (*n*) electrons are considered non-degenerate we need substitute expressions appropriate for *nf* only, those for *n* being negligible. Thus from (4) and (5) we get the well-known formula

$$n_f = G.\frac{(2\pi mkT)^{\frac{3}{2}}}{h^3}e^{-\frac{\chi}{kT}}$$

but for the spin factor G.

Actually, however, the electrons outside the metal are sparse and non-degenerate, whereas inside the metal they are tight-packed and degeneracy is of dominant importance. Thus we must substitute in (4), expression (6) for nf and (7) for n and we have

$$nf=\beta e^{-\frac{\chi}{kT}+\frac{h^2}{2mkT}\left(\frac{3n}{4\pi G}\right)^{\frac{2}{3}}-\frac{\pi^2}{12}\frac{mkT}{h^2}\left(\frac{4\pi G}{3n}\right)^{\frac{2}{3}}}$$

$$=G\,\frac{(2\pi mkT)^{\frac{3}{2}}}{h^3}\,e^{-\frac{\chi}{kT}+\frac{h^2}{2mkT}\left(\frac{3n}{4nG}\right)^{\frac{2}{3}}-\frac{\pi^2}{12}\frac{mkT}{h^2}\left(\frac{4\pi G}{3n}\right)^{\frac{2}{3}}}$$

which is identical with that obtained by Fowler[2] by the method of partitions.

Though of no practical importance, the formula in the case when both the electron systems are supposed degenerate is also deducible easily from (4) and (7). In this case we obtain

$$\frac{h^2}{2mT}\cdot\left(\frac{3n_f}{4\pi G}\right)^{\frac{2}{3}}-\frac{\pi^2k^2mT}{h^2}\left(\frac{4\pi G}{3n_f}\right)^{\frac{2}{3}}$$

$$-\frac{h^2}{2mT}\left(\frac{3n}{4\pi G}\right)^{\frac{2}{3}}+\frac{n^2k^2mT}{12h^2}\left(\frac{4\pi G}{3n}\right)^{\frac{2}{3}}=-\frac{\chi}{T}$$

(2) Chemical equilibria :—

Let us restrict our discussions to reactions involving three systems only in which systems 1 and 2 react to form system 3. When all of them are non-degenerate, considering unit Volume, we get by substitution of (6) in (4) for each of them, due regard being given for signs,

$$-k\log\frac{n_1}{\beta}-k\log\frac{n_2}{\beta}+k\log\frac{n_3}{\beta}=-\frac{\chi}{T}\,.$$

$$\text{or}\ \frac{n_3}{n_1n_2}=G\,\frac{(2\pi mkT)^{\frac{3}{2}}}{h^3}\,e^{-\frac{\chi}{kT}}$$

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[2] Fowler, Proc. Roy. Soc., Vol. 117, 549 (1928).

It will be noticed that there is a small discrepancy between this and Fowler's result since the latter obtains an extra factor 2 in the third term of the index of e.

which is the well-known formula of Ehrenfest and Trkal,[3] got by the method of γ-weight when all the systems are degenerate we obtain similarly

$$\frac{h^2}{2m\mathrm{T}}\left(\frac{3}{4\pi\mathrm{G}}\right)^{\frac{2}{3}}\left[n_3{}^{\frac{2}{3}}-n_1{}^{\frac{2}{3}}-n_2{}^{\frac{2}{3}}\right]$$

$$+\frac{\pi^2k^2m\mathrm{T}}{h^2}\left(\frac{4\mathrm{G}\pi}{3}\right)^{\frac{2}{3}}\left[\frac{1}{n^{\frac{2}{3}}_1}+\frac{1}{n^{\frac{2}{3}}_2}-\frac{1}{n^{\frac{2}{3}}_3}\right]=-\frac{\chi}{\mathrm{T}}\,.$$

The corresponding formula for the case in which any one of the systems is degenerate and the rest non-degenerate follows easily and need not be further discussed here. Our formula, moreover, is capable of giving the value of chemical equilibrium constant, for equilibria involving any number of systems by very simple substitutions in (4).

As a particular case of the above, we may consider the ionization formula of Saha where the electrons constitute a degenerate system, the atoms and positive ions being non-degenerate. Since Chandrasekhar's formula is a little faulty we give the corrected formula below

$$k_1\log\frac{n_+}{n}+\left(\frac{3n_-}{4\pi\mathrm{G}}\right)^{\frac{2}{3}}\frac{h^2}{2m\mathrm{T}}-\frac{\pi^2k^2m\mathrm{T}}{12h^2}\left(\frac{4\pi\mathrm{G}}{3n_-}\right)^{\frac{2}{3}}=-\frac{\chi}{\mathrm{T}}$$

(3) The Vapour pressure of a crystal can also be calculated likewise. But degeneracy in this case is never met with, so that we content ourselves by giving the classical, statistical Result

$$n=\mathrm{G}\,\frac{(2\pi mk\mathrm{T})^{\frac{3}{2}}}{h^3}\,e^{-\frac{\chi}{k\mathrm{T}}}$$

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[3] Tolman's ' Statistical Mechanics with special applications to Physics and Chemistry," p 184.

which is the same as the formula of Stern and Tetrode, but for the spin factor G.

In conclusion I wish to express my sincere thanks to Sir C. V. Raman and Prof. B. Venkatesachar for their kind help and suggestions.

19

On the Raman Spectra of Di-methyl Ether, Di-ethyl Ether and Heptane

By

S. C. SIRKAR.

(Plate XXII.)

(*Received for publication, 10th May, 1932.*)

ABSTRACT.

The Raman Spectra of di-methyl ether, di-ethyl ether and heptane have been examined in order to clear up some doubtful points. The following frequencies have been observed.

Di-methyl ether :—333 (0), 416 (0), 921 (2), 1102 (0), 1454 (1*b*), 2814 (7), 2869 (3), 2921 (3), 2952 (3) and 2989 (3).

Di-ethyl ether :—375 (0), 440 (5), 494 (0), 844 (3), 928 (0*b*), 1030 (0), 1077 (0), 1151 (2), 1272 (0*b*), 1453 (3), 2695 (1), 2802 (1½), 2865 (6), 2931 (6) and 2979 (4).

Heptane :—304 (2), 398 (2*b*), 441 (2), 541 (2), 769 (4), 843 (2), 900 (2*b*), 962 (3*b*), 1031 (2), 1080 (2*b*), 1135 (1*b*), 1161 (2), 1242 (1*b*), 1263 (2*b*), 1301 (3), 1338 (1), 1450 (5*b*), 2651 (1), 2704 (2), 2854 (8*b*), 2922 (6*b*) and 2958 (4*b*).

In the case of di-methyl ether, two new lines 333 (0) and 416 (0) are recorded. The latter agrees fairly with one of the frequencies calculated on the assumption that the molecule conforms to a triangular model. In the case of di-ethyl ether, it has been possible, with the help of a quinine sulphate filter, to clear up some doubts as regards the assignment of some of the lines and five out of six hydrogen frequencies recorded by Bär have been confirmed. The results have been discussed in relation to the infra-red data.

1. *Introduction.*

In continuation of the work started by Dr. Krishnamurti[1] about the critical investigation of the Raman spectra, the author[2] has recently reported the results for a few liquids. A few more organic liquids have been examined with suitable technique in order to record the fainter lines and to assign the lines correctly. The results are reported and discussed in relation to infra-red spectra in the present paper.

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[1] P. Krishnamurti, Ind. Jour. Phys., 6, 367 (1931)

2. *Experimental Results.*

The liquids chosen for the present investigation are heptane, di-methyl ether and di-ethyl ether. Heptane was fractionated before being exposed in order to settle the question whether a large number of the lines recorded by Ganesan and Venkateswaran[3] and not recorded by Bonino and Brüll[4] are really due to some impurity. Two spectrograms were obtained for this liquid, one with uranine and another with 0-cresolphthalein light filter, in order to clean up the region after 4358 A° and to assign the lines correctly. In the case of diethyl ether one spectrogram was obtained without using any filter and another with quinine sulphate filter in order to get rid of excitation by 4046 A° and thus assign the frequencies correctly. Kahlbaum's ether distilled in vacuum was used. Di-methyl ether was received from the manufacturers as gas dissolved in sulphuric acid sealed up in a big capsule. The gas was liquefied with the help of liquid air in a strong glass tube. In this case a long exposure was given without any filter. Iron arc spectrum was photographed on each plate for comparison. A Fuess glass spectrograph having a dispersion of about 15 A° per mm. in the region of 4358 A° was used. The results are given in the Tables I, II and III. Complete tables showing assignment will be found at the end of the paper.

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[2] S. C. Sirkar, Ind. Jour. Phys., 7, 61 (1932).

[3] A. S. Ganesan and S. Venkateswaran, Ind. Jour. Phys., 4, 196 (1929).

[4] G. B. Bonino and L. Brüll, Gazz. Chim. Ital., 59, 660 (1929).

TABLE I.

Heptane Frequencies.

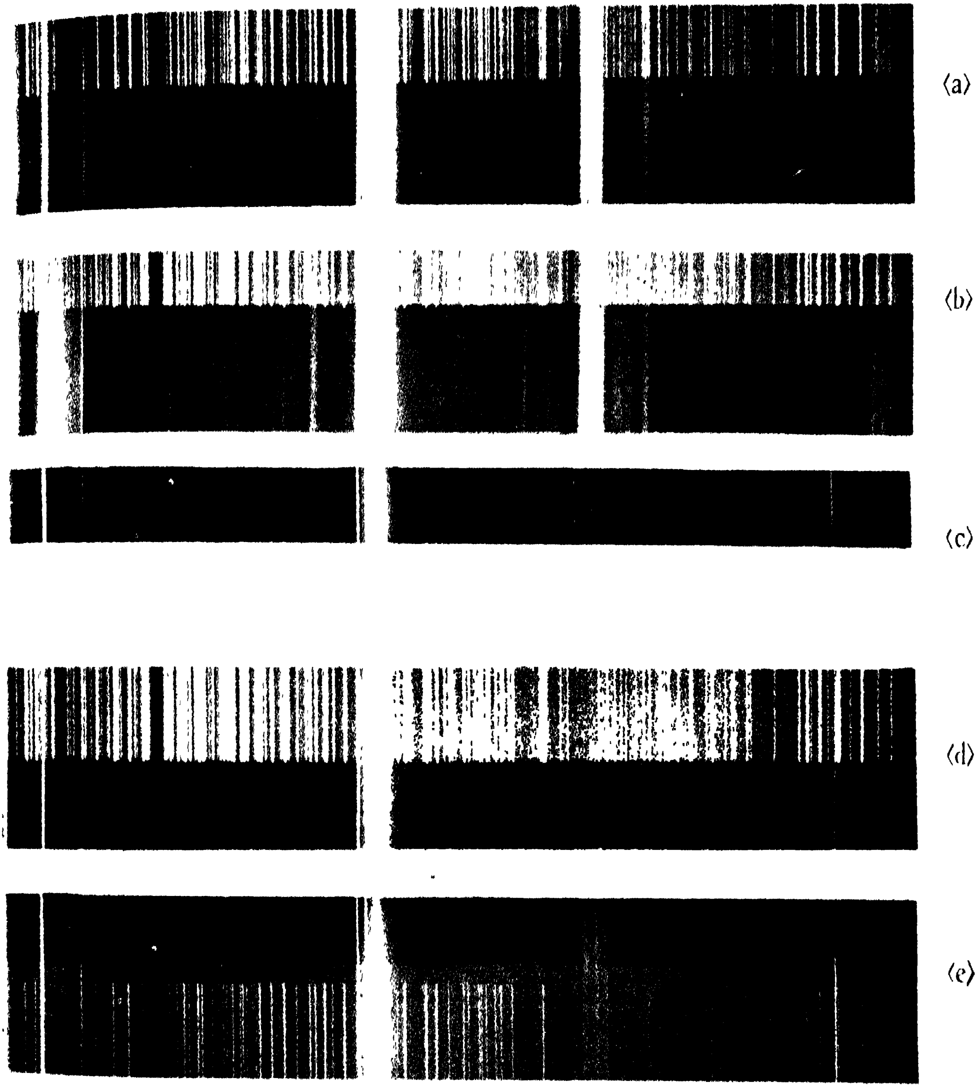
Number.	$\Delta\nu$.	Intensity.	Values in μ.	Infra-red Max μ.
1	304	2	32·9	
2	398	2 (*b*)	25·13	
3	441	2	22·68	
4	541	2	18·48	
	...	...	...	14·0
5	769	4	13·0	13·1
6	843	2	11·87	
7	900	2 (*b*)	11·11	11·0
8	962	3 (*b*)	10·40	10·45
9	1031	2	9·71	
10	1080	2 (*b*)	9·26	
11	1135	1 (*b*)	8·81	
12	1161	2	8·61	8·65
13	1242	1 (*b*)	8·05	
14	1263	2 (*b*)	7·92	
15	1301	3	7·69	
16	1338	1	7·47	
	...	...	...	7·2
17	1450	5 (*b*)	6·90	
	...	...	...	5·8
18	2651	1	3·77	
19	2704	2	3·70	
20	2854	8 (*b*)	3·50	
21	2922	6 (*b*)	3·42	3·4
22	2958	4 (*b*)	3·38	

Bonino and Brüll but recorded by Ganesan and Venkateswaran are observed by the author. These lines are therefore genuine lines due to heptane and not due to any impurity. The spectrogram is reproduced in Plate XXII and it can be seen that these lines are quite intense. The line 154 recorded by previous workers was not observed on the author's plate. Similarly the lines 274 (0), 346 (1), 499 (0), 720 (0) and 1400 (1) recorded by Ganesan and Venkateswaran could not be observed on the author's plate though the plate was free from continuous background and at the same time well exposed. The hydrogen frequencies 2651

Table IV.

Heptane.

Bonino and Brüll.	Ganesan and Venkateswaran.	Sirkar.	Bonino and Brüll.	Ganesan and Venkateswaran.	Sirkar.
154 (1)	147 (1)			1132 (0)	1135 (1*b*)
	274 (0)			1162 (1)	1161 (2)
	312 (1)	304 (2)		1244 (1)	1242 (1*b*)
	346 (1)			1266 (1)	1263 (2*b*)
	407 (1)	398 (2*b*)		1304 (2)	1301 (3)
	447 (1)	441 (2)		1348 (2)	1338 (1)
	499 (0)			1400 (1)	
	546 (1)	541 (2)	1448 (3)	1453 (3)	1450 (5*b*)
	720 (0)				2651 (1)
765 (2)	769 (3)	769 (4)		2853 (4)	2704 (2)
822 (2)	845 (2)	843 (2)	2865 (5)	2872 (3)	2854 (8*b*)
897 (1)	903 (2)	900 (2*b*)		2912 (3)	2922 (6*b*)
956 (1)	967 (2)	962 (3*b*)	2932 (5)	2931 (4)	2958 (4*b*)
1027 (1)	1034 (3)	1031 (2)		2963 (3)	
	1088 (1)	1080 (2*b*)			



(a) Heptane (O-cresolphthalein filter)

(b) Heptane (uranine filter)

(c) Dimethyl ether.

(d) Di-ethyl ether (Quinine filter)

(e) Di-ethyl ether (without filter)

and 2704 are new and genuine because they were found to be excited by 4358A and falling in a region of the spectrum where there was no confusion due to the presence of many other lines. The wave-lengths were quite different from those of the mercury bands in this region. The lines 2872 and 2931 recorded by Ganesan and Venkateswaran were not found well resolved on the author's plate because the neighbouring hydrogen lines were very intense and broad.

The infra-red absorption curve for heptane is not given by Cobtentz but Bonino and Brüll have quoted the wave-lengths of the absorption peaks observed by Lecomte.[7] These are given in Table I. It is interesting to compare the Raman spectra as well as the infra-red spectra of heptane and octane with each other because both molecules are of the form of long chains one differing from the other only by a CH_2 link. The octane frequencies recorded recently by Krishnamurti[8] are plotted graphically in Fig. 1 along with those of heptane. It can be seen from the figure that though most of the frequencies of the two compounds are almost identical, each has got a few frequencies not common to both. If it is assumed that the carbon

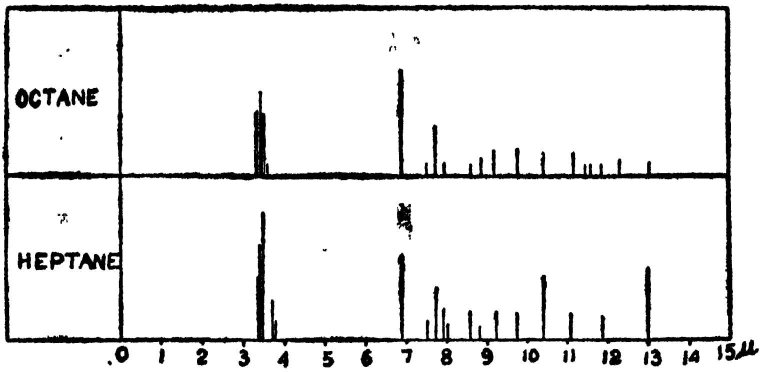


Fig. 1.

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[7] Lecomte, Contribution a l'etude de l'absorption des Rayons Infra rouges etc., Paris, 1924.

[8] P. Krishnamurti, Ind. Jour. Phys., 6, 543 (1931).

atoms are arranged in a staggered chain in both the molecules, it is evident that the elements of symmetry of the two molecules are quite different. If the symmetry elements of the length of the molecule are taken into consideration, it will be found that in the case of octane there is only one centre of symmetry whereas heptane has one twofold axis of rotation perpendicular to the molecule and passing through the middle carbon atom. The distances of the carbon atoms from the centre of the molecule are different for the two molecules. The low frequencies may be attributed to the different modes of vibration of the length of molecule and for the reasons given above, frequencies of some modes of vibration are quite different in the two cases. Some of the hydrogen frequencies also, are different in the two cases on account of the symmetry elements being different.

Di-ethyl Ether.

Di-ethyl ether was studied formerly by Ganesan and Venkateswaran.[9] Daure,[10] Dadieu and Kohlrausch[11] and others. The frequencies recorded by various authors are tabulated in Table V. It can be seen from the table that most of the lines observed by the author are in confirmation of the work of the previous authors. The faint line 375 was not recorded by any of the previous workers and is a genuine new line. The lines 2695 and 2802 recorded only by Bär[12] previously are confirmed by the author. A glance at Table VII will show how the quinine sulphate filter has helped very much in the correct assignment of these lines. The lines at 4542·2A and 4564·3A are quite strong on the plate obtained without any filter but they are very weak on the plate obtained with quinine filter

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[9] A. S. Ganesan and S. Venkateswaran, Ind. Jour. Phys., 4, 196 (1929).

[10] P. Daure, Ann. de Phys., 12, 375 (1929).

[11] A. Dadieu and K. W. F. Kohlrausch, Wien Ber., 138, 635 (1929); 139, 677 (1929).

[12] R. Bär, Helv. Phys. Acta., 4, 366 (1931).

TABLE V.

Di-ethyl Ether.

Daure.	Ganesan and Venkateswaran.	Dadieu and Kohlrausch.	Bär.	Sirkar.
				375 (0)
436 (2)	441 (3)	436 (5)	434 (4)	440 (5)
		510 (1)	493 (?)	494 (0)
	798 (0)			
835 (2)	845 (3)	845 (5)	840 (3)	844 (3)
922 (1 br)	928 (2)	928 (3)	927 (1b)	928 (0b)
	1027 (1)	1037 (4)		1030 (0)
1090 (4 br)	1082 (0)			1077 (0)
	1150 (1)	1147 (3)	1148 (3)	1151 (2)
	1197 (0)			
	1263 (1)	1276 (4 br)	1270 (2b)	1272 (0b)
	1334 (1)		1352 (?)	
1448 (2 br)	1457 (2)		1454 (5 br)	1453 (3)
			1478 (?)	
			2692 (1)	2695 (1)
			2730 (0)	
			2806 (2)	2802 (1½)
2858 (3 br)	2871 (6)		2866 (8b)	2865 (6)
2926 (4 br)	2936 (6)		2930 (10)	2931 (6)
2973 (3 br)	2977 (6)		2978 (4)	2979 (4)

though the other lines excited by 4358A are stronger on the latter plate than on the former. These lines are therefore excited by the line 4046A. But it can be seen that on each of these lines there is superposed a line excited by 4358A, because on the quinine filter plate these lines are present and almost as intense as the other strong hydrogen lines 2865, 2931 and 2979. Had these lines 4542·2A and 4564·3A been excited by 4046A alone on the quinine filter plate, their intensities would be much less than those of the lines 2865, 2931 and 2979. Since that is not the case, the lines 928 and 1030 excited by 4358A are also superposed on these lines respectively. The lines 928 and 1030 are found to be excited also by the line 4046A and are therefore genuine. Similarly the line 1077 being excited by both 4358A and 4046A is genuine. The lines 1030 and 1077 have not been recorded by Bär. Out of the six hydrogen lines 2692 (1), 2730 (0), 2806 (2), 2866 (8b), 2932 (10) and 2980 (4) recorded by Bär only five were observed on the author's plates and the line 2730 could not be observed. The existence of this line is doubtful or at least it is much less intense than the line 2802.

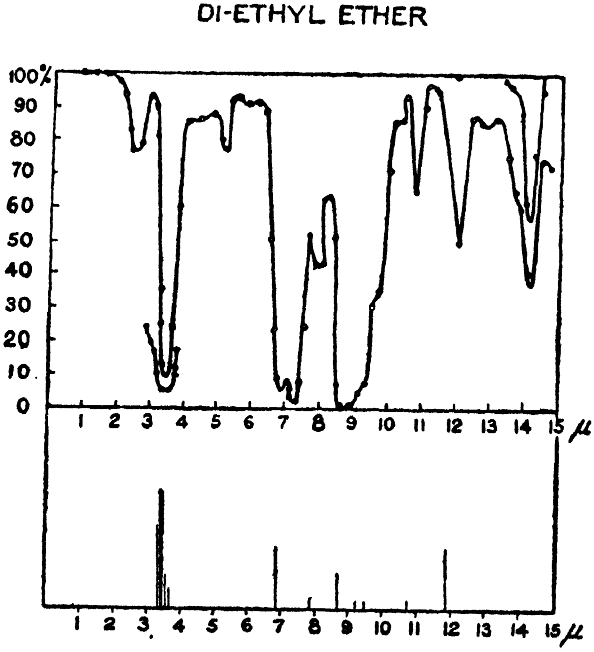

Fig. 2.

The infra-red absorption curve given by Coblentz[13] is reproduced in Fig. 2 along with the Raman lines. It can be seen that most of the frequencies obtained in the Raman spectrum are active and are represented by absorption peaks. The relative intensities of the absorption peaks however, are quite different from those of the Raman lines as is expected from theorectial point of view because the intensities of Raman lines depend on changes in polarisability and those of absorption peaks on electric moments induced during a transition from one vibrational level to another and these properties have no connection with each other.

Di-methyl Ether.

Di-methyl ether was studied formerly by Dadieu and Kohlrausch in the liquid state. Two new lines 333 (0) and 416 (0) are observed by the author besides all the lines recorded by the previous authors.

If a triangular model of the di-methyl ether molecule is assumed and masses proportional to 16, 15 and 15 are supposed to be situated at the vertices of the triangle, the three characteristic frequencies of vibration of such a model can be obtained after assuming some reasonable values for the binding forces, in the method given by Dadieu and Kohlrausch.[14] If f_1 and f_2, the forces of restitution between $O-CH_3$ and CH_3-CH_3 groups be taken as $4{\cdot}8\times10^5$ and $1{\cdot}5\times10^5$ dynes per cm. respectively, the following frequencies are obtained.

$$\nu_1=1102,\quad \nu_2=1035,\quad \nu_3=420,\quad \alpha=53^\circ-42'$$

The observed frequencies are

$$\nu_1=1102,\quad \nu_2=921,\quad \nu_3=416$$

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[13] W. W. Coblentz, Investigations of Infra-red Spectra, Carnegie Institution, Washington, 1905, p. 172.

[14] A Dadieu and K. W. F. Kohlrausch., Wien. Ber., 139, 165 (1930).

If any other frequency, *e.g.*, 921, be taken as ν_1 no reasonable values for ν_2 and ν_8 are obtained.

When f_1 is taken as 5×10^5 dynes cm. as given by Dadieu and Kohlrausch for $HO-CH_3$, ν_8 becomes 461 with f_2 as $1{\cdot}66 \times 10^5$ dynes cm. A very low value of f_2 has to be assumed in that case to get agreement with the observed value for ν_8. If the line 333 be taken as ν_3, still lower value of f_2 has to be assumed.

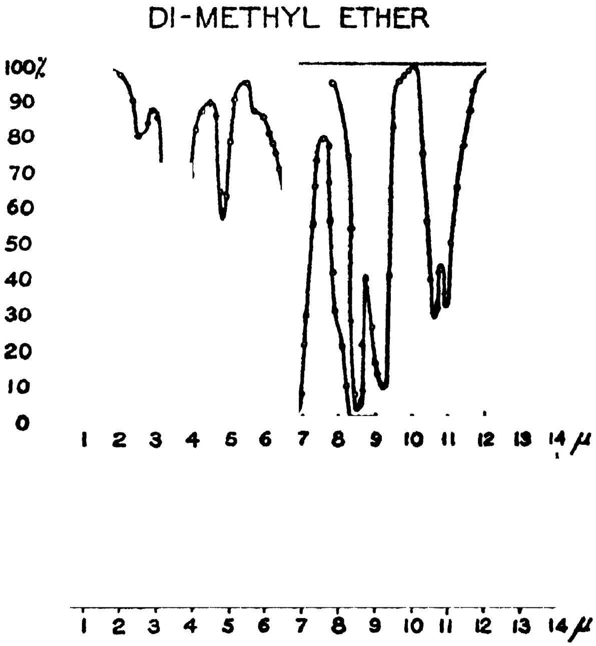

Fig. 3.

The infra-red absorption curve for di-methyl ether given by Coblentz[15] is reproduced in Fig. 3 along with the Raman lines. As in the case of di-ethyl ether most of the frequencies are represented by absorption peaks but there is no correspondence between relative intensities of the Raman and infra-red spectra.

The author is indebted to Prof. Sir C. V. Raman, F.R.S., for his kind interest and guidance in the present work

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[15] W. W. Coblentz, *loc. cit.*, p. 171.

TABLE VI.

Heptane.

Wave length of Raman line in I.A.	Wave number ν.	Intensity.		Assignment.
		Uranine filter.	O-Cresolph. filter.	
4120·3	24263·3	2	—	B–442
4137·7	24161·2	2	—	B–544
4176·75	24135·3	4	—	B–770
4189·8	23860·8	1	—	B–845
4199·5	23805·7	1(b)	—	B–900
4210·6	23742·9	1(b)	—	B–963
4222·7	23674·9	2	—	B–1031
4231·5	23625·7	2(b)	—	B–1080
4241·5	23570	1(b)	—	B–1135
4246·1	23544·4	2	—	B–1161
4260·8	23463·2	1(b)	—	B–1242
4264·21	23444·5	2(b)	—	B–1261
4271·8	23402·8	3	—	B–1303
4278·2	23367·8	1	—	B–1338
4299·1	23254·2	5(b)	—	B–1451
4416·9	22634	1½	2	A–304
4435·3	22540	1½(b)	2(b)	A–398
4443·8	22497·0	1½	2	A–441
4463·6	22397·2	1½	2	A–541
4509·5	22169·2	3	4	A–769
4524·6	22095·2	1½	2	A–843
4536·25	22038·5	1½(b)	2(b)	A–900
4549·1	21976·2	2(b)	3(b)	A–962
4563·4	21907·4	1½	2	A–1031
4573·67	21858·2	10	7	B–2847 A–1080
4576·7	21843·7	5	3	B–2862

TABLE VI.

Heptane (continued).

Wave length of Raman line in I.A.	Wave number ν.	Intensity.		Assignment.
		Uranine filter.	O-Cresolph. filter.	
4589·4	21783·3	7 (*b*)	5 (*b*)	B—2922
4596·8	21748·2	5 (*b*)	3 (*b*)	B—2957
4612·3	21765·1	2 (*b*)	2 (*b*)	A—1263 B—2841
4620·4	21637·1	1½	2	A—1301
4629·73	21593·5	2	1	b_1—2922
4637·2	21558·7	1	½	b_1—2957
4652·3	21488·7	3 (*b*)	5 (*b*)	A—1449
4927·9	20287	0	½	A—2651
4940·8	20234	½	1	A—2704
4977·8	20083·6	3 (*b*)	5 (*b*)	A—2854
4994·5	20016·5	2½ (*b*)	4 (*b*)	A—2922
5003·5	19980·4	2 (*b*)	3 (b)	A—2958

TABLE VII.

Di-ethyl Ether.

Wave lentgh of Raman line in I.A.	Wave number ν.	Intensity.		Assignment.
		Without filter.	Quinine filter.	
4119·8	24266·2	2	—	B—439
4189·5	23862·5	1½	—	B—843
4204·5	23777·4	0 (*b*)	—	B—928
4222·5	23676	0	—	B—1030
4231·2	23627·3	0	—	B—1078
4244·6	23552·7	1	—	B—1153
4266·5	23431·8	½	—	B—1274
4299·5	23252	2	—	B—1453
4430·8	22563	0	0	A—375
4443·6	22498	3	5	A—440
4454·3	22444	0	—	A—494
4524·8	22094·2	2	3	A—844
4542·2	22009·6	1	0 (*b*)	B—2696 A—928
4563·2	21908·3	—	0 (*b*)	A—1030
4564·3	21903	1½	—	B—2802
4573·1	21861	—	0	A—1077
4577·5	21840·8	5	½	B—2865
4588·5	21787·5	½	1½	A—1151
4591·2	21774·7	5	½	B—2931
4601·5	21726	3	0	B—2979
4614·3	21665·7	½	1	A—1272
4617·5	21650·7	0	—	b_1—2865
4631·8	21583·8	0	—	b_1—2932
4641·0	21541	0	—	b_1—2975
4653·1	21485	2	3	A—1453
4980·1	20074·4	1½	2	A—2863
4996·5	20008·4	1½	2	A—2930
5008·5	19960·5	1	1½	A—2978

TABLE VIII.

Di-methyl Ether.

Wave length of Raman line in I.A.	Wave number ν.	$\Delta\nu$.	Intensity.	Assignment.
4202·87	23786·6	919	1	B
4235·5	23603·3	1102	0	B
4299·64	23251·2	1454	1 (*b*)	B
4422·6	22604·8	333	0	A
4438·8	22522·3	416	0	A
4540·66	22017	921	2	A
4566·8	21891	2814	8	B
4578·31	21836	2869	3	B
		1102		A
4589·27	21783·9	2921	3	B
4595·7	21753·3	2952	3	B
4603 5	21716·4	2989	2 (*b*)	B
4652·8	21486·4	1452	1 (*b*)	A
4967·9	20123·6	2815	3	A
4981·5	20068·7	2869	1	A
4994·13	20018	2920	½	A
5001·9	19986·9	2951	½	A
5012·07	19946·3	2992	½ (*b*)	A

TABLE IX.

Exciting Lines.

Symbol used.	Wave length in I.A.	Wave number.	Intensity.
A	4358·34	22938·1	10,000
a_1	4347·5	22995·3	600
b_1	4077·84	24515·9	700
B	4046·56	24705·4	7,000

210, BOWBAZAR STREET,
CALCUTTA.

20

New Lines in the Absorption Spectra of the Alkalies

By

Dr. Snehamoy Datta and Birendrakumar Chakravarty.

(Plate XXIII.)

(*Received for publication, 6th May, 1932.*)

Abstract.

Absorption Spectra of K, Na, and Rb have been photographed at moderate pressures. Besides the absorption lines of the Principal Series some new lines on both sides of the former have been observed. The difference in wave-number between these lines and the corresponding principal absorption lines agrees fairly well with the difference in the vibration levels of the molecules expressed in wave-numbers. The new lines can be expressed by an equation of the type $\nu_n = [{}^2S_{1/2} - m\,{}^2P_{3/2,\ 1/2}] + \triangle\nu$ where $\triangle\nu$ measures the difference in wave-number corresponding to the various vibrational transitions of the molecules. A tentative explanation is given.

1. *Introduction.*

According to the modern Spectral Theory the valence electrons of the alkalies in the normal state are in the ${}^2S_{1/2}$ orbit. Hence according to the Bohr Principle of Selection the absorption spectrum of a cool alkali vapour should exhibit only the Principal Series ${}^2S_{1/2} - m^2P_{3/2,\ 1/2}$ as absorption lines.

Long ago one of us (Proc. Roy. Soc., Vol. 101, Sec. A, 1922) observed besides the absorption lines of the principal series several new lines in the case of potassium of which no traces could be found at low pressures. These lines seemed to have no correspondence with the emission lines of potassium and attempts to correlate them were not successful.

With a view mainly to improve existing measures which might throw additional light regarding the nature of these absorption lines as also to see whether this type of absorption is peculiar to potassium alone or is traceable in the case of other alkalies, the original experiment with potassium was repeated with an instrument of larger dispersion and subsequently extended to sodium as well as rubidium.

2. *Experimental.*

The experimental arrangement was one of usual type. The vapour was allowed to form in a steel tube (about 20 inches long with an internal diameter of one inch) with quartz end pieces fixed to the tube with pitch, the ends being kept cool by circulation of cold water through the jackets provided at the ends. The tube was heated in a gas furnace whereby its temperature could be raised up to about 1000°C. A sufficient quantity of the pure metals was introduced into the tube in order to maintain a high pressure of the vapour and the tube was perfectly evacuated by a Cenco-Hyvac air pump before being heated. The temperature and thereby the pressure of the vapour could be controlled by adjusting the pressure of the flame.

Photographs were taken in the first order of a 15 ft. Concave Grating which gives a dispersion of about 2·3 A.U. per mm. in the regions studied. The absorption spectrum of the vapour was photographed in the centre of the photographic plate with iron comparison spectra on both sides of it. Exposure given in each case was from one to two hours. As the source of light in experiments with potassium and rubidium the positive crater of a carbon arc was employed and in case of sodium for which the region λ2500 to λ2900 had to be photographed, the carbon arc being unsuitable, was replaced by a mercury arc of the atmospheric type which gives quite a strong continuous background in this region.

For the carbon arc the electrodes were treated in nitric acid to remove the metallic impurities (specially iron). It was run on a current of 7 amperes from 220 volts mains. The length of the arc was maintained as small as possible. The mercury arc was run on a current of 2 amperes from 220 volts supply.

The carbon arc besides giving out a strong continuous spectrum emitted a few iron and other lines, which were used with advantage as comparison lines and provided the surest check against any mechanical shift. The measurement of wave-lengths was made as usual. The error involved in such measurement did not exceed 0·01 A.U.

3. *Observations.*

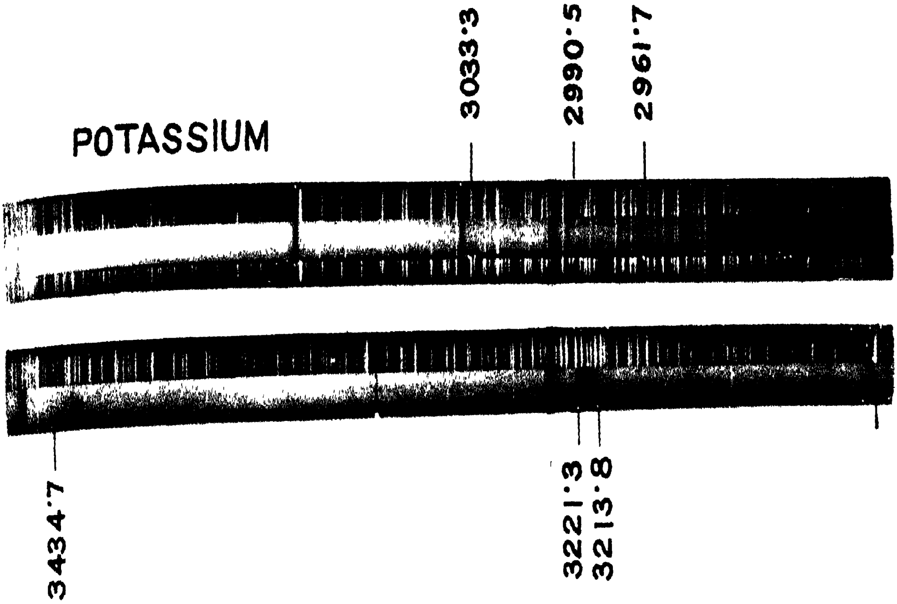
Potassium :—Photographs were taken in the region λ2900 to λ3500. The new absorption lines are observed from $m=3$ to $m=14$ (see Plate). Corresponding to $m=3$ there is only one line on the longer wave-length side of the principal absorption line. For $m=4$ and $m=5$ there are lines on both sides of the principal absorption lines. These lines are rather broad and diffuse. For $m=6$ towards higher members each principal absorption line is associated with a new absorption line on the shorter wave-length side only. The lines become fainter as the higher members are approached and finally disappear. For $m=2$ also, there are new lines but these cannot be distinguished from bands occuring in that region which are developed even at a comparatively lower pressure. The new lines corresponding to the higher members appear only when the pressure is sufficiently high, colour of the transmitted light being deep green.

Sodium :—Photographs were taken in the region λ2500 to λ3300. The new absorption lines are observed for $m=5, 6, 7$. No such lines in case of $m=2, 3, 4$ could be observed owing to the fact that the corresponding regions were masked by innumerable bands which could not be got rid of at the pressure necessary for the production of these lines. The new lines observed are in each case on the shorter wave-length side of the corresponding principal absorption lines. The yellow part of the spectrum (corresponding to the D-lines) was examined with an eyepiece. When the pressure was high, innumerable bands were developed on both sides of the D-lines but by gradually diminishing the pressure of the vapour by lowering the temperature of the furnace a stage was reached when there were no bands. On a critical observation it was found that at this stage there were two faint lines on both sides of the D-lines which existed for a short time after the bands disappeared. This stage of affair was however momentary and so no attempt was made to photograph them. These lines seemed to have the same origin which accounts for the appearance of the other new lines. In case of sodium the new lines are rather sharp as compared to those in the case of potassium where the lines are blurred. It was found that there was a critical pressure for which the new lines in sodium were more prominently developed. The pressure necessary for such a purpose was much less than that in case of potassium.

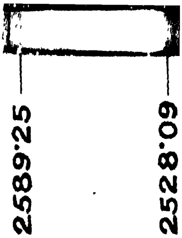
Rubidium :—In the case of rubidium the lines are somewhat blurred as in potassium and they are more prominently developed at a comparatively higher pressure. New lines observed are from $m=5$ to $m=11$. For $m=5$ and 6 the lines are observed on both sides of the principal lines. From $m=7$, each principal absorption line is associated with a faint absorption line on the longer wave-

PLATE XXIII

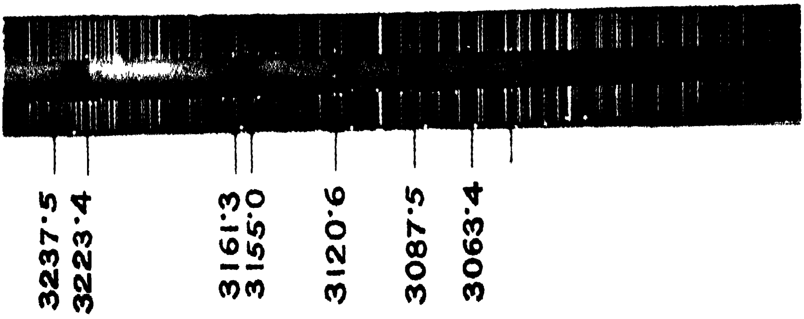
POTASSIUM



SODIUM



RUBIDIUM



length side only. The new lines corresponding to the higher members are however too faint for any accurate wave-length measurement.

Experimental Results.

TABLE I—Potassium.

λ (air) I.A.	λ (vac.) I.A.	ν_n (vac.) New lines.	ν_p (vac.) Principal Lines.	$(\nu_n - \nu_p)$.
3434·7	3433·7	29106·2	28996·6 (3)	109·6
3221·3	3222·3	31034·7	31069·8 (4)	−35·1
3213·8	3214·7	31107·1	31069·8 (4)	37·3
3105·8	3106·7	32188·5	32227·7 (5)	−39·2
3100 5	3101·4	32243·5	32227·7 (5)	15·8
3033·3	3934·2	32957·6	32940·1 (6)	17·5
2990·5	2991·4	33429·2	33410·1 (7)	19·1
2961·7	2962·6	33754·1	33736·8 (8)	17·3
2941·2	2942·1	33989·3	33972·3 (9)	17·0
2926·1	2927·0	34164·7	34164·7 (10)	17·0
2914·5	2915·4	34300·6	34282·2 (11)	18·4
2905·7	2906·6	34404·5	34387·3 (12)	17·2

The lines corresponding to the 13th and 14th members of the principal series are too faint for any accurate wave-length measurement. The lines corresponding to the 4th and 5th members are broad and diffuse and their wave-length measurements are not very certain.

TABLE II—Sodium.

λ (air) I.A.	λ (vac.) I.A.	ν_n (vac.) New lines.	ν_p (vac.) Principal Lines.	$(\nu_n - \nu_p)$.
2502·35	2503·11	39950·3	39793·6 (7)	156·7
2528·09	2528·85	39543·7	39298·3 (6)	245·4
2589·25	2590·03	38609·6	38540·1 (5)	69·5

TABLE III—Rubidium.

λ(air) I.A.	λ(vac)I.A.	ν_n(vac). New lines.	ν_p (vac) Principal Lines.	$(\nu_n-\nu_p)$.
3237·5	3238·5	30878·5	30959·2 (5)	−80·7
3223·4	3224·4	31013·5	30959·2 (5)	54·3
3161·3	3162·2	31624·6	31655·3 (6)	−30·7
3155·0	3155·9	31686·7	31655·3 (6)	31·4
3120·6	3121·5	32035·9	32115·8 (7)	−79·9
3087·5	3088·4	32379·2	32434·2 (8)	−55·0
3063·4	3064·3	32664·9	32695·9 (9)	−31·0

The wave-numbers of the principal series lines of potassium have been taken from the list of absorption lines given by Datta (Proc. Roy. Soc., Sec. A, Vol. 101, p. 541, 1922) and those of sodium and rubidium from Fowler's "Report on Series in Line Spectra" pp. 99 and104.

Discussion of Results.

The wave-lengths of the new lines are collected in the first column and their divergences from the nearest principal lines in wave-numbers are shown in the last column of each table. These differences show a striking agreement with the wave-numbers calculated from the possible vibrational transitions of the corresponding molecules which have been calculated in the case of potassium and sodium from the gross structure analysis of potassium and sodium bands by Fredrickson and Watson (Physical Review, Vol. 30, p. 429, 1927) where the band heads have been found to satisfy the following equations:

Red K_2. : $\nu=15368{\cdot}63+(74{\cdot}58n'-0{\cdot}30n'^2)-(92{\cdot}01n''-0{\cdot}31n''^2)$
Red Na_2: $\nu=15006{\cdot}68+(115{\cdot}69n'\text{-}0{\cdot}427n'^2)-(157{\cdot}81n''-0{\cdot}538n''^2)$
Green Na_2: $\nu=20301{\cdot}62+(123{\cdot}84n'-0{\cdot}79n'^2)-(157{\cdot}57n''-0{\cdot}57n''^2)$.

From these formulæ the possible vibration levels of the molecules in the intial and final states for an electronic transition can be schematically drawn. Figures I and II(*a*), II(*b*) give such schematic representations of the possible vibration levels for the K_2 and Na_2 molecules respectively and the wave-numbers corresponding to possible transitions are shown along the arrow indicating the particular transition.

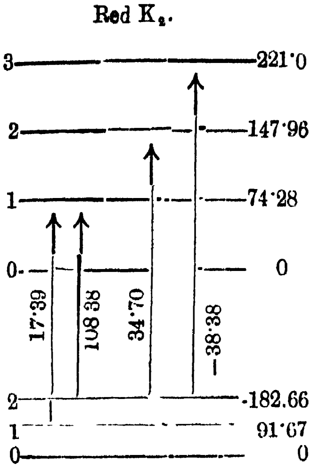


Fig. I.

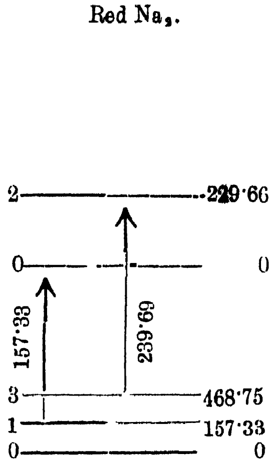


Fig. II (*a*).

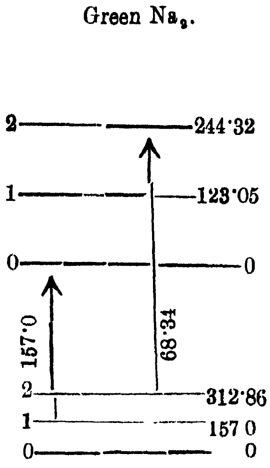


Fig. II (*b*).

The wave-number of the new lines can thus be expressed by an equation of the type:

$$\nu_n = {}^2S_{1/2} - m\,{}^2P_{3/2,\ 1/2} + \triangle\nu$$

where $\triangle\nu$=difference in wave-number corresponding to the various vibrational transitions of the molecules.

There is no known band spectrum of rubidium so that our results with rubidium cannot be directly verified. However from the nature of the values of $\triangle\nu$ obtained, it may be suggested that the appearance of these lines is also due to the same cause which accounts for the new lines in the absorption spectra of potassium and sodium vapour.

Conclusion.

Although the separation of the new lines from the associated principal lines are in remarkable agreement with the vibrational transitions of the corresponding molecules, it is difficult to see how the vibrational energy differences of the *molecules* (and not the energy corresponding to the fundamental vibration frequency) are superposed on the electronic transition of the *atoms* during absorption. Had the observation been confined to potassium alone one might have been inclined to regard this agreement as a pure accident but its confirmation in the case of sodium and the fact that similar lines also appear in rubidium irresistibly leads one to the conclusion that there must be something significant about the observed agreement.

The phenemenon observed may be tentatively explained by somewhat modifying the idea of transference of energy from one system to another by 'collisions of the second kind' which was first introduced by Klein and Rosseland (Z. Phy., 4, 46, 1921) and subsequently very successfully extended by Franck (Z. Phy., 9, 259, 1922) to explain a number of phenomena such as the quenching of Resonance radiation, Sensitised Fluorescence, etc. Now in all these cases the collision either adds or subtracts an amount of energy by which the system is transferred from one quantised to another quantised level. It is further known that when the energy difference between two such levels correspond to a transition in the vibrational energy of the bombarding molecule the said transference is more effective (Oldendurg—Z. Phy. 49, 609, 1928).

If we now assume that the vibrating alkali molecules, which are also present in the chamber, set up a perturbation in the atomic orbits by collision or otherwise, then one can conceive of the perturbed atoms thereby gaining an amount of energy equal to the vibration energy of the molecule, *viz.*, $h.\,n'w_0$, (w_0 being the vibration frequency of the molecule), although there is no quantised level admitting such a change.

Leaving aside the small amount of perturbation due to rotation, which will practically broaden the line this hypothesis would mean that when the alkali atoms are in their normal state ${}^2S_{\frac{1}{2}}$, their energy is modified by $\triangle\nu$ in wave-numbers, where $\Delta\nu = n'w_0$, w_0 being the frequency of vibration of the molecules in the excited state. The incident light is now absorbed by the atoms which would thereby be raised to $m^2P_{\frac{3}{2}}$, $\frac{1}{2}$ states under ordinary circumstances but as the atoms in these excited states would also come into collision with the molecules the energy corresponding to these states would be that appropriate to $m^2P_{\frac{3}{2}}$, $\frac{1}{2}$ states together with the perturbations caused by the molecules. If this be $\triangle\nu$ as before, the quanta that will be actually absorbed by the atoms will be the same as without the presence of the molecules, *viz.*,

$$\nu=\left[{}^2S_{\frac{1}{2}}+\triangle\nu\right]-\left[m^2P_{\frac{3}{2}},{}_{\frac{1}{2}}+\triangle\nu\right]={}^2S_{\frac{1}{2}}-m^2P_{\frac{3}{2}},{}_{\frac{1}{2}}$$

and the ordinary principal series lines will be absorbed. If however, the vibrational energy of the molecules change somehow say to a value $\triangle\nu'$ the corresponding amount of perturbation of the atomic energy for some of the atoms would be $\triangle\nu'$ and the quanta that will be actually absorbed will be the one expressed by the equation :—

$$\nu=\left[{}^2S_{\frac{1}{2}}+\Delta\nu\right]-\left[m^2P_{\frac{3}{2}},{}_{\frac{1}{2}}+\triangle\nu'\right]$$

$$=\left[{}^2S_{\frac{1}{2}}-m^2P_{\frac{3}{2}},{}_{\frac{1}{2}}\right[+[\triangle\nu-\triangle\nu']$$

resulting in the displacement of the line by an amount $[\Delta\nu-\triangle\nu']$ from the corresponding principal line.

Now in the circumstances in which the experiments with the alkali vapours are performed the molecules are also thrown into the excited state as is revealed by the appearance of a strong banded absorption in the red and green and the vibrational energy of the molecules are thereby changed from $\triangle\nu = n'w_0$ to $\triangle\nu' = n''w'_0$. Thus the excited atoms would come into collision with not only the cool molecules which will not effect any change in the line absorption but would also come into contact with excited molecules which would produce a modification of the absorption line in the manner stated above and this would account for the appearance of new lines in the absorption spectra of the alkalies. As the proportion of such excited molecules is rather low and the life of the excited molecules very short this would explain the faintness of these lines and also the fact that for their appearance a rather high pressure would be necessary.

If the assumption outlined above is true then similar lines are expected to appear in the presence of other foreign gases with whom the absorbing atoms do not form a compound provided that the molecules of the foreign gas are also thrown into excited state by the incident light. Experiments are in progress to test this hypothesis.

Presidency College,
Calcutta.
The 6th May, 1932.

A New Steel Flooring

The development of a new steel flooring after long scientific investigation has been announced by Mellon Institute of Industrial Research, Pittsburgh, Pa. This flooring consists of slabs, 24 inches wide and up to 12 feet 5 inches in length at present, that are fabricated by preforming two steel sheets and subsequently welding them together in the plane above the neutral axis. A cross-section taken through the width of a completed unit shows four keystone-shaped cells, all connected together near the neutral axis. These four ducts, which constitute each unit, are spaced at six-inch intervals and connect directly, when installed, with the corresponding ducts of the adjacent section of floor slab. This arrangement is described as enabling the utilization of the new floor not only as an efficient load-carrying member, but also as a multiple floor-duct system for handling all types of electrical lines. Such a grouping of parallel cells with six-inch spacing is claimed to permit, at any time, the installation of electrical outlets within a radius of three inches from the exact location required, thus providing permanent electrical flexibility and precluding electrical obsolescence.

It is said that the keystone slab can be installed with ease and rapidity ; that it can be bolted, clipped, or welded into place across the structural members, affording a working floor for the various trades. This floor is fire-safe ; it is adaptable to appropriate finishes and to suspended ceilings and service piping, and has a low weight per square foot.

21

The Raman Spectra of Iodides, Part I, Phosphonium Iodide and Methyl Iodide.

BY

N. GOPAL PAI.

(Plate XXIV.)

[*Received for publication, 11th May, 1932.*]

ABSTRACT.

The Raman effect in *crystals of phosphonium iodide* has been studied with a view to correlate it with the crystal structure of the compound. The frequencies found are 930 (2), 1040 (0), 1113 (0), 1259 (1), 1416 (1), 2304 (10), 2370 (8). All these frequencies are attributed to the ionic group PH_4 found in the crystal which is assumed to be distorted under the influence of the neighbouring iodine ions.

The Raman spectrum of methyl iodide liquid has been studied thoroughly, the method of continuous distillation[1] being used to avoid the effect of photo-chemical decompositon. The following thirteen frequencies, of which five are being reported for the first time have been established :—

524 (8), 895 (1), 1028 (0), 1242 (3), 1434 (1), 1760 (0), 2050 (0), 2461 (1), 2557 (1), 2796 (1), 2849 (1), 2950 (5), and 3050 (3).

Allowing for the small diminution of frequency which occurs in passing from the vapour to the liquid state, every one of the Q branches observed in the infra-red absorption of the vapour by Bennet and Meyer[2] has a corresponding Raman line.

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[1] N. N. Pal and P. N. Sengupta, Ind. J. Phys., 5, 609 (1930).

[2] Willard H. Bennet and Charles F. Meyer. Phys. Rev., 32, 888 (1998).

1. *Phosphonium Iodide.*

Crystals of phosphonium iodide supplied by Kahlbaum in sealed tubes were used. They were of fairly large size and had a faint yellow tint though they were of 'pure' quality. One of the unopened tubes was used in the experiment. Light from a mercury lamp was focussed by a powerful condenser on the centre of the tube and the scattered light examined by a Fuess glass spectrograph of high dispersion. On using Ilford Isozenith plates (speed No. 700 H & D), which were backed before use, it was found that 48 hours of exposure was enough to bring out all the lines including the weaker ones. The plates were measured on a Hilger micrometer and the wave-length of the lines were calculated by using the simplified form of Hartman's interpolation formula, with the known mercury lines as standards. The wave numbers (in vac. per cm.) were calculated and the shifts in wave numbers of the Raman lines from the corresponding exciting lines determined. The following table represents the results of the analysis. The exciting lines are 4046·6 and 4358·3 and are represented by the letters *d* and *h* respectively.

TABLE I.

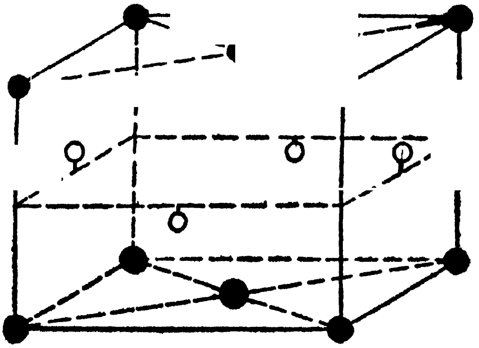
I.	ν.	$\Delta\nu$.	Remarks.
10	22401	*d*—2304	Sharp, strong
8	22338	*d*—2367	Diffuse
2	22008	*h*—930	Sharp, faint
0	21893	*h*—1040	Faint
0	21825	*h*—1113	Faint
1	21679	*h*—1259	Diffuse
1	21522	*h*—1416	Diffuse
10	20634	*h*—2304	Sharp, strong
8	20568	*h*—2370	Diffuse

$\Delta\nu$=930 (2), 1040 (0), 1113 (0), 1259 (1), 1416 (1), 2304 (10), 2370 (8).

Another exposure was given only for 12 hours with a fairly strong aqueous solution of quinine sulphate on the path of the incident rays which diminished the intensity of the Raman lines arising from 4046·6. The results thus obtained confirmed the assignments shown in Table I.

2. *Discussion.*

Crystals of phosphonium iodide are cube-like in appearance, but have been shown to be tetragonal and the cube-like habit has been attributed to combination of (110) and (001). The study of crystal structure of this compound by Dickinson[8] revealed that the arrangement of the phosphorous and iodine atom is as shown in the figure where the black circles represent the phosphorous atoms and the white circles represent the iodine atoms. As a result of a small displacement of the iodine atom from the exact centre, each phosphorous atom instead of having 8 iodine atoms equidistant from it, has four, at a distance which is different from the distance of the remaining four. In so far as no grouping of the phosphorous and iodine atoms could be made, the structure has been considered ionic.



As is well known, the distinct difference between the ionic and molecular lattice finds a counterpart in the Raman spectra. While typical molecular crystals show the Raman lines very prominently, ionic crystals such as NaCl give no lines or only extremely faint lines which are in fact so weak that their appearance is explained as due to a second order effect namely the lattice of sodium ions oscillating against the lattice of chlorine ions. From the X-ray investigations, PH_4I has to be considered an ionic crystal and may be expected to exhibit in scattering only the lines due to the internal oscillations within the ion PH_4. We cannot, under the experimental conditions described, expect such a weak effect as the lattice oscillation to manifest itself distinctly. Secondly the lattice oscillations due to such massive and ionic system as the phosphonium *ion* and the iodine *ion* should be of fairly low frequency (as could be easily seen by a comparative study) of the order of 100 wave numbers. In the results obtained, there is no line of such low frequency. The data from scattering thus appears to be consistent with the structure of the crystal inferred from X-ray measurements.

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[8] Roscoe, G. Dickinson—J. Ann. Chem. Soc., XLIV, 1489 (1922).

It would be of interest to compare the data with the infra-red data available in the case of phosphine. This was thoroughly studied by Robertson and Fox[4] who assigned 676·7, 993.2 and 1125 as the fundamental frequencies. Badger and Mecke[5] after a critical study of the results and comparing it with the results deduced in the case of ammonia, concluded that the fundamentals of PH_3 are $\gamma_1 = 2327$; $\gamma_2 = 1125$ and $\gamma_3 = 993 \cdot 2$. It is very probable however that there is also a fourth fundamental which has been overlooked in the analysis. The appearance of the two lines 2304 and 2370 in the scattering by phosphonium iodide confirms the view that PH_3 possesses at least one fundamental frequency in the vicinity of these lines. Accepting this view, we have a rough correspondence between the Raman frequencies for PH_4I and the infra-red fundamentals of PH_3. The values for PH_4I (Table II) are slightly less than the corresponding values for PH_3. This result is analogous to the shifts[6] of frequency observed in passing from SO_3 to SO_4 (Table III).

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[4] R. Robertson and J. J. Fox, Proc. Roy. Soc., A. Vol. 120, p. 128 (1928).

[5] R. M. Badger and R. Mecke, Zeits. f. Phys. Chem., 5, Abt. B, p. 333 (1929).

TABLE II.

Infra-red data for PH_3 gas.	Scattering for $[PH_4]I$ solid.	Dif.
993	930	63
	1040	...
1125	1113	12
...	1259	...
...	1416	...
2327	2304	23
...	2370	...

TABLE III.

SO_3	SO_4	Dif.
534	450	84
...	614	...
1068	989	79
1403	1218	185

In the case of the four frequencies, 1040, 1259, 1416 and 2370 of PH_4I, there is no corresponding value in the infra-red data for PH_3.

Accepting the view that all the lines recorded for PH_4I, are due to the ion $(PH_4{}^+)$ we may divide them into four groups, namely, 930, the weak pair 1040 and 1113, the strong pair 1259 and 1416 and the very strong pair 2304 and 2370. The 930 line stands by itself being the sharpest of all, but of low intensity. The pair 1040 and 1113 are both very weak and diffuse and in fact might easily be overlooked on the plate except on a careful examination. The pair 1215 and 1416 are of identical appearance and intensity. The pair 2304 and 2370 similar in possessing great intensity, differ in the fact that 2304 is sharp while 2370 is diffuse, the former being more intense. This natural division has one point against it, in so far as it does not, according to the well-known facts isolate the single intense and sharp line which is attributed to the symmetrical expansion and contraction of the tetrahedron.

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[6] S. Bhagavantam, Ind. Jour. Phys., 5, 93 (1930).

If the configuration of the (PH_4^+) group be a perfect tetrahedron, it would have four fundamental frequencies. A distorted tetrahedron would have nine fundamental frequencies which could be grouped by comparison with the case in which the distortion vanishes as 2 (doublet) 3 (triplet) 1 single and 3 (triplet) forming nine lines in all.

The structure obtained by placing in a unit of dimensions $6{\cdot}34 \times 6{\cdot}34 \times 4{\cdot}62$ Å, phosphorous atoms at (000) and $(\frac{1}{2}, \frac{1}{2}, 0)$ and the iodine atoms at $(0, \frac{1}{2}, u)$ and $(\frac{1}{2}, 0, \bar{u})$ where u is close to 0·40 is observed to explain the X-ray data of this compound satisfactorily. Consistent with the symmetry of the phosphonium iodide arrangement, the hydrogen atoms also may be grouped round the phosphorous atom to occupy the equivalent positions (corresponding to the space group, D_{4h}^{7},)

$$(uov)\ (\bar{u}ov)\ (o\bar{u}v)\ (o\bar{u}\bar{v}),\ (\tfrac{1}{2}+u,\ \tfrac{1}{2},\ v)\ (\tfrac{1}{2}-u,\ \tfrac{1}{2},\ \bar{v})\ (\tfrac{1}{2},\ \tfrac{1}{2}+u,\ v)$$
$$(\tfrac{1}{2},\ \tfrac{1}{2}-u,\ v),$$

where u and v may have values from 0 to 1. If the exact value of u and v is known, the shape of the tetrahedron is determined. Because of the low mass of hydrogen atoms, X-ray data fail to give any information about this. It is possible to attribute such values to u and v and make the resulting tetrahedron a regular one, but the probability is that the tetrahedron is a distorted one. This appears to be more correct if the nature of arrangement of the iodine atoms round the phosphorous atom is considered. Since the iodine atoms are arranged round any phosphorous atom not as a group of eight, but as two groups of four, the distortion of the (PH_4)

under these different forces is inevitable. The frequencies obtained may accordingly be classified as

$$\left.\begin{array}{c}930\\ \\1040\end{array}\right\} \quad \begin{array}{c}1113\\1259\\1416\end{array}\Big\} \quad 2304 \text{ and } 2370.$$

The 2370 frequency may be a close triplet which is not sufficiently well resolved and is seen to be a single line. Another possible explanation is to assume that the tetrahedron is distorted only to that extent to produce only these 7 frequencies.

A study of the polarisation of lines in a solution of phosphonium iodide in a suitable solvent will show which of these two is the correct assignment.

The symmetrical expansion and contraction of the tetrahedron causes the 2304 frequency. Compared with the results obtained from other similar compounds as methane, the tetrachlorides of carbon, silicon, tin, etc.,[7] this assignment appears to be justifiable. Thus in the case of CCl_4 of the four frequencies,

$$217, \quad 313, \quad 459 \quad \left\{\begin{array}{l}760\\ \\791\end{array}\right.$$

the Raman frequency of 459 has properties identical with those of the line under consideration and this has been attributed to a similar type of oscillation. The most recent results obtained by Bhagavantam[8] with another similar hydride—methane—are seen to confirm this view. Frequencies 1304, 1520, 2918, 3018 are taken as the fundamentals of this molecule and the line 2918 singled out from others because of its sharpness and intensity. This too has been ascribed to a symmetrical expansion and contraction of the tetrahedron.

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[7] Bhagavantam—*Loc. cit.*

[8] S. Bhagavantam—Ind. Jour. Phys. VI, 595 (1932).

The remaining lines may be identified with the other three modes of vibration of a tetrahedron. Thus, the line at 2370 and $\left\{\begin{matrix}1113\\1259\\1416\end{matrix}\right.$ can be ascribed to the two different modes in which the central atom moves within the tetrahedron. The $\left\{\begin{matrix}930\\1040\end{matrix}\right.$ frequency may correspond to one in which the hydrogen atoms move about transversely.

3. *Methyl Iodide.*

The procedure recommended by Pal and Sengupta[9] is used here. As a result of the continuous distillation that is made to go on during the exposure, the photochemical decomposition which causes the liquid to become brownish or yellow is prevented and the plate obtained is free from continuous spectrum. An exposure of 24 hours brought out all the strong lines. The plate showed indications of the presence of certain feeble lines, and accordingly, a long exposure of 120 hours was given to bring out these strongly. Golden Isozenith plate, (speed 1400 H & D) was used and was backed before use. The experimental procedure for the measurement of the plate is the same as for phosphonium iodide. The following table gives the result of analysis. The intensities of the Raman lines (I) their wave-numbers (ν) and the shifts in wave numbers ($\triangle\nu$) are given under the respective columns. The incident exciting lines 3650·1; 3654·8; 3663·3; 4046·6; 4077·8; 4339·5; 4347·5 and 4358·3 are represented by the letters, *a*, *b*, *c*, *d*, *e*, *f*, *g* and *h* respectively.

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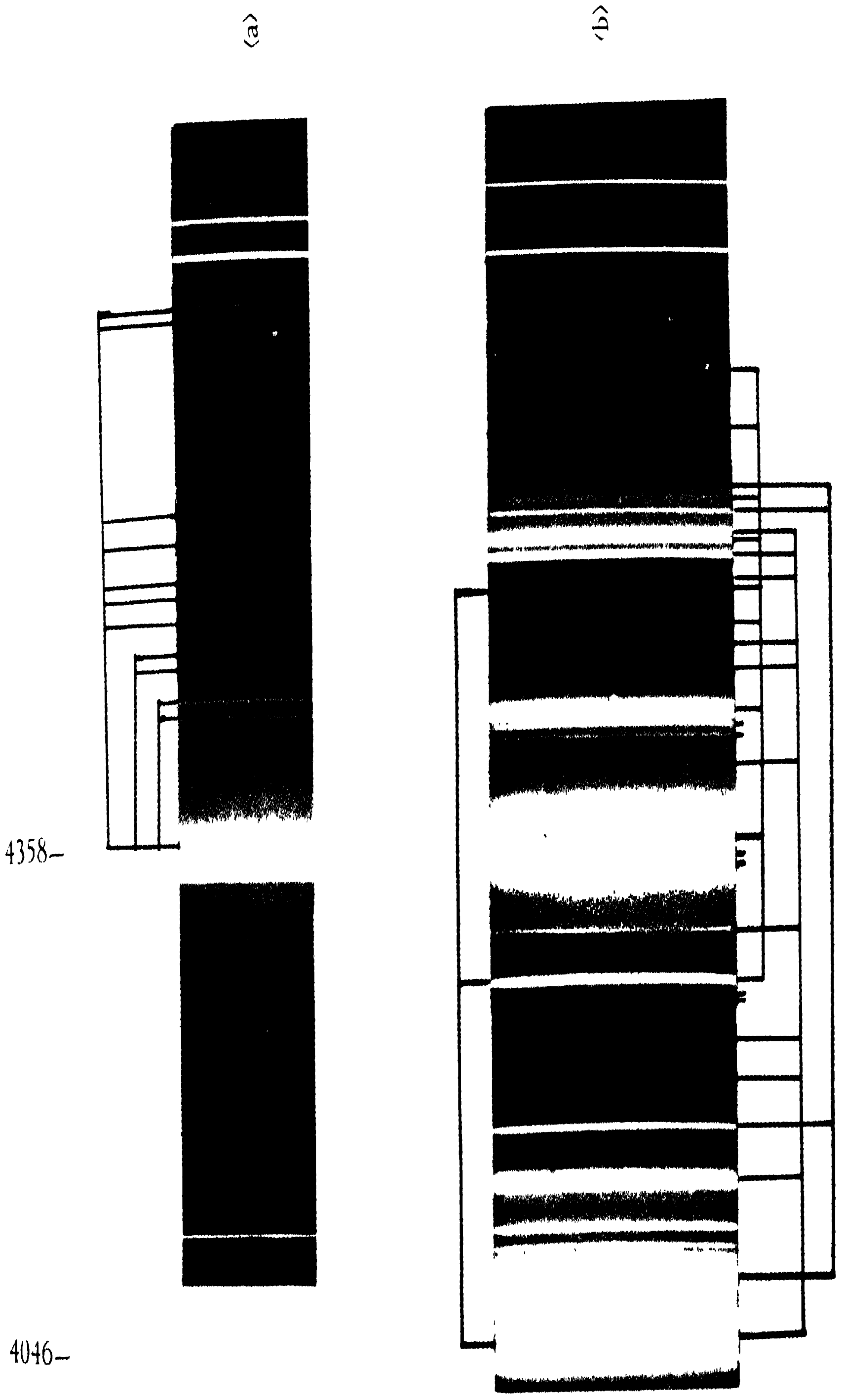
[9] Pal and Sengupta—*Loc. cit.*



Raman Spectra

(a) Phosphonium iodide ; (b) Methyl iodide

TABLE IV.

I.	Wave No. ν.	Δν.	I	Wave No. ν.	Δν.
2	25229	d + 524	1	22472	g − 523
0	25040	e + 524	8	22416	h − 522
3	24440	a − 2049	1	22244	d − 2461
3	24404	b − 2950	1	22148	d − 2557
0	24241	b − 3049	1	22042	h − 896
8	24181	d − 524	1	21909	d − 2796 h − 1029
4	23991	e − 525			
1	23811	d − 894	1	21856	d − 2849
0	23678	d − 1027	5	21755	d − 2950
1	23566	f + 527	3	21698	h − 1240
1	23518	g + 523	3	21654	d − 3051
5	23461	h + 523 d − 1244	3	21566	e − 2950
			1	21506	h − 1436
1	23272	d − 1433	1	21460	e − 3056
0	22655	d − 2050	0	21178	h − 1760
1	22516	f − 523	0	20887	h − 2051

Δν = 524 (8); 895 (1); 1028 (0); 1242 (3); 1434 (1); 1760 (0);
2050 (0); 2461 (1); 2557 (1); 2796 (1); 2849 (1);
2950 (5); 3050 (3).

To help the identification of various lines, an exposure for 120 hours with a ortho-cresolphthalein filter on the path of the incident rays was taken in which, it was seen that the lines due to 4046 were weakened considerably or were completely cut out. Besides diminishing the intensity of 4046, this filter wipes out the faint mercury bands present in the neighbourhood of 4797 A.U. thereby helping us to detect any Raman line that may be present in this region.

4. *Discussion.*

The Raman spectra of this compound has been investigated by various workers including Dadieu-Kohlrausch,[10] Ball,[11] Cleeton and Dufford.[12] A comparison of the results of the various investigators is included along with the infra-red frequency data available. Coblentz[13] studied the infra-red absorption spectra of methyl iodide in the liquid state while Bennett and Meyer investigated the vapour up to 14 μ. Recently, Sleator[14] investigated the infra-red absorption data of the compound in vapour state, beyond this region—up to 20 μ approximately and observed a new band at 18·78 μ. The results obtained are in fair agreement. Only the Q branch of the band is referred to, neglecting the fine structure of the band.

A comparison of the Raman spectra of the substance with the infra-red data reveals certain interesting details.

The infra-red absorption data for vapour are taken from Bennett and Meyer's tables excepting 532 which is from Sleator's work. The infra-red absorption data for liquid is from Coblentz's " Investigations of Infra-red spectra."

The varous frequencies recorded, correspond to various modes of oscillation of the molecule. These modes of oscillation may be divided into two types : those in which the electric moment vibrates parallel to the axis of symmetry of the molecule, and the second type, in which the vibration of the electric moment is perpendicular to the axis of symmetry. The former produces the band of the $\|^1$ type and the latter is responsible for the band of the $\perp^r$ type. The frequencies at

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[10] A. Dadieu & K.W.F. Kohlrausch, Wien. Ber. *139*, 77 (1930).
Do. Wien. Ber. *139*, 717 (1930).

[11] G. N. Ball, Z. f. Phys., *66*, 257, (1930).

[12] C. D. Cleeton & R. T. Dafford, Phys. Rev., *37*, 362 (1931).

[13] Coblentz, " Investigations of Infra-red spectra."

[14] W. W. Sleator, Phys. Rev., *38*, 147, (1931).

TABLE V.

Ball.	Cleeton-Dufford.	Dadieu-Kohlrausch.	Pai.	Infra-red frequency.	
				Vapour.	Liquid.
509	534	522	524	532 $\parallel^{l}$	
					668
					717
					813
			895	885 $\perp^{r}$	885
					935
			1028		1026
					1087
1248	1254	1239	1242	1252 $\parallel^{l}$	1217
		1416	1434	1446 $\perp^{r}$	1408
			1760		1695
					1852
			2050		
					2174
			2461		
	2589		2557		
	2771		2796		
		2889	2849	2861 $\parallel^{l}$	
2953	2946	2947	2950	2970 $\parallel^{l}$	2940
	3036	3046	3050	3074 $\perp^{r}$	

2950, 2849, 1242 and 524 belong to the first type while those at 3050, 1434 and 895 represent the second type. These three frequencies 3050, 1434 and 895 appear in descending order of intensity in scattering, the 895 being a very weak line. In the infra-red however, this happens to be the most intense absorption band, the 1434 coming second in order of magnitude, and the 3050 being feeble. In the case of the four frequencies classed under the first type, there is no such order to be noticed. In the first place, there is the 1242 frequency, which has manifested strongly in the infra-red absorption while in scattering also, it has come out as a fairly strong line. In the case of the 524 line, it appears as an intense line in scattering, while in the infra-red it is only a feeble band.

As a contrast to this type of frequency, there are two sharp lines at 1028 and 2050 which are weak both in scattering and in the infra-red absorption.

The remaining four frequencies, 1760, 2461, 2557 and 2796 have no correspondence with the infra-red absorption data. They all appear as diffuse and feeble lines.

Just as there is a good correspondence between the infra-red absorption data for the monohalogen substituted derivatives of methane, the correspondence is found to be present in the scattering also. The following table shows the result at a glance.

A critical study of this table reveals that the Raman data in all these cases except for methyl iodide are very incomplete. A thorough investigation in the case of the other halides is sure to throw more light on the subject.

The author's best thanks are due to Prof. Sir C. V. Raman at whose suggestion the work was taken up, for his keen interest and kind guidance.

TABLE VI.

Methane.		Methyl fluoride.		Methyl chloride.		Methyl bromide.		Methyl iodide.	
Scattering.	Infra-red. gas.	Scattering.	Infra-red vapour.	Scattering in liquid.	Infra-red vapour.	Scattering in liquid.	Infra-red vapour.	Scattering in liquid.	Infra red vapour.
	1304		1049	712	732	594	615	524	532
			1200	1098	1019		957	895	885
								1028	
			1476		1355	1296	1306	1242	1252
	1520				1460		1451	1434	1446
								1760	
								2050	
								2461	
								2557	
								2796	
			2862	2815	2880		(2862)	2849	2861
2918			2965	2955	2967	2956	(2973)	2950	2971
3018	3013		2987	3024	3047	3050	3062	3050	3074

22

The Spark Spectrum of Arsenic

By

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Abstract.

Accurate data for the spark spectrum of arsenic, which has so far been lacking, is provided in the visible and near ultraviolet regions. In all about 130 lines have been measured, majority of which are new. The experimental arrangements suggest that the lines are probably due to singly ionised arsenic.

The spark spectrum of arsenic has been studied by a number of investigators,[1] mainly by the methods of passing condensed discharge between arsenic electrodes and in giessler tubes. Both these methods appear to be unsuitable for obtaining lines in the red, visible and ultraviolet regions. The electrodeless discharge provides a satisfactory source for producing lines in these regions. In this paper altogether 130 lines have been tabulated from 5651·29 to 3780·80 most of which have been observed for the first time and evidence is in favour of the view that these belong to As^+.

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[1] Kayser's Handbuch der Spektroskopie, Vol, VII, p. 62.

Experimental.

Arsenic was placed in a pyrex glass tube about 40 cms. long and 2 cms. diameter and at the ends were sealed glass windows. The tube was connected to a mercury diffusion pump for exhaustion, and was surrounded by a coil of 8 or 9 turns, through which a condensed discharge was passed. The tube was then heated moderately but continuously close to the coil, and as the arsenic began to volatilise, a brilliant greenish ring of light characteristic of arsenic made its appearance. The pressure of the arsenic vapour was not kept very low. This was a great advantage as the impurity lines were almost entirely cut off and even the strongest mercury line remained absent. The light was focussed on the slit of a 3-metre concave grating mounted after the method of Paschen and Runge. Iron lines were used as standards for comparison.

Lines in the first order spectrum were measured though one plate in the second order was also taken. A Hilger photo-measuring micrometer was used for measurements. The wave-lengths are given in the accompanying table and are believed to be correct to within ·02 Angstrom units.

I am very thankful to the authorities of the Science College, Patna, particularly Prof. Mukerjee, Head of the Physics Department, who allowed me to take the photographs on the concave grating fitted up in the Laboratory, and provided necessary facilities.

I must also tender my sincerest thanks to Dr. P. K. Kichlu of the Lahore Government College who suggested this problem and gave me help and guidance during the progress of the work.

λ (I.A)	Int.	ν (Vac)
5651·29	(6)	17690·20
5558·05	(6)	17986·9
5497·73	(5)	18184·3
5331·28	(5)	18752·0
5231·30	(2)	19110·4
5107·58	(5)	19573·8
5105·64	(3)	19580·7
4985·42	(2)	20052·9
4888·44	(2)	20450·7
4879·73	(3)	20487·2
4860·76	(0)	20567·2
4847·79	(1)	20622·2
4805·94	(4)	20801·8
4802·54	(0)	20816·5
4799·41	(2)	20830·1
4787·06	(0)	20883·9
4764·84	(2)	20981·2
4735 97	(3)	21109·1
4730·79	(4)	21132·2
4727·05	(1)	21148·9
4707·75	(4)	21235·7
4672·77	(2)	21394·6
4658·34	(1)	21460·9
4632·92	(1)	21578·6
4630·30	(3)	21590·8
4628·08	(3)	21601·2
4610·15	(4)	21685·2
4607·76	(3)	21696·5
4603·04	(4)	21718·8

λ (I.A.)	Int.	ν (Vac.)
4591·41	1	21773·7
4590·61	2	21777·5
4581·50	0	21820·8
4580·08	1	21827·6
4553·02	4	21957·3
4549·87	5	21972·5
4546·02	2	21991·1
4544·25	5	21999·7
4540·71	5	22016·8
4533·20	2	22053·3
4529·54	1	22071·1
4526·94	2	22083·8
4510·18	1	22165·9
4508·86	2	22172·4
4495·62	5	22237·7
4483·20	1	22299·3
4476·95	1	22330·4
4475·87	3	22335·8
4467·81	5	22376·1
4462·61	2	22402·1
4461·69	1	22406·8
4460·04	5	22415·1
4458·30	1	22423·8
4433·32	4	22550·2
4431·98	2	22557·0
4428·97	4	22572·3
4427·81	4	22578·2
4422·76	2	22604·0
4415·41	3	22641·6
4414·15	2	22648·1

λ (I.A.)	Int.	ν (Vac.)
4406·34	1	22688·2
4403·04	3	22705·2
4402·18	1	22709·7
4376·88	2	22840·8
4371·09	4	22871·2
4362·21	1	22917·7
4355·50	1	22953·0
4354·82	4	22956·6
4350·73	5	22978·2
4339·50	3	23037·7
4334·05	2	23066·6
4326·86	2	23105·0
4318·76	2	23148·3
4305·25	1	23220·9
4302·64	1	23235·0
4300·58	1	23246·2
4280·71	1	23354·1
4269·94	0	23413·0
4269·47	1	23415·5
4265·24	0	23438·8
4252·07	1	23511·4
4245·50	3	23547·7
4230·56	3	23630·9
4229·06	2	23639·3
4227·79	1	23646·4
4223·32	1	23671·4
4211·68	1	23737·1
4209·92	2	23746·8
4202·37	0	23789·4
4199·27	3	23807·0

λ (I.A.)	Int.	ν (Vac.)
4191·88	2	23848·9
4161·42	0	24023·5
4158·77	1	24038·8
4132·79	0	24189·9
4120·66	2	24261·1
4104·75	1	24355·2
4102·16	2	24370·6
4084·64	1	24475·1
4083·04	2	24484·7
4072·68	1	24546·9
4065·91	2	24587·8
4063·30	1	24603·6
4061·35	0	24615·4
4055·81	0	24649·1
4043·56	0	24723·7
4037·47	6	24761·0
4032·72	4	24790·2
4031·45	5	24798·0
4014·12	2	24905·1
4010·75	1	24926·0
4009·24	2	24935·4
4006·35	3	24953·4
3994·66	1	25026·4
3982·21	0	25104·6
3948·48	3	25319·1
3946·07	1	25334·5
3930·97	2	25431·8
3928·59	1	25447·3
3922·35	5	25487·7
3914·38	0	25539·6

λ (I.A.)	Int.	ν (Vac.)
3883·06	3	25745·6
3871·11	2	25825·1
3868·22	1	25844·4
3861·47	2	25889·6
3854·37	1	25937·2
3850·42	2	25963·9
3842·33	4	26018·5
3840·72	0	26029·4
3804·21	0	26279·2
3786·68	2	26400·9
3782·61	1	26429·3
3780·80	0	26441·9

Transmission of Light through Suspensions of Powdered Crystals

By

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Palit Research Scholar in Physics.

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ABSTRACT.

The problem of transmission of light through a suspension of randomly orientated particles is worked out. The expression obtained shows in agreement with experiment a much smaller transmission for a suspension of doubly refracting particles than for those of an isotropic body. It is further shown that if the incident light is polarised, the transmitted light is also completely polarised, but it is overlaid by an admixture of strong scattered or diffused light which is unpolarised.

1. *Introduction.*

In a well-known experiment, Christiansen[1] showed that powdered glass which is ordinarily white and opaque may be made transparent for any desired region of the spectrum by immersing it in a mixture of liquids having a suitably adjusted refractive index. The theory of this phenomenon has been very fully discussed by Drs. Sethi[2] and Sogani.[3] Sethi reported that if the powdered substance is a doubly refractive solid, *e.g.*, quartz, the suspension does not actually become transparent for any part of the spectrum when the refractive index of the liquid is varied, but merely diffuses light to a greater or less extent. On the other hand, some recent workers namely Procopiu[4] and Petrescu[5] report that light is transmitted by suspensions of crystalline powders in liquids, and further claim that if the incident light is plane polarised, the light transmitted by the suspension is partially depolarised. These statements are evidently conflicting, and the present investigation was undertaken with a view to elucidate the problem of the transmission of light through a suspension of randomly orientated crystalline particles.

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[1] Ann. der Physik, 23 (1884).

[2] Proceedings of the Ind. Assoc. for Cult. of Sc., 6, 136 (1920-21).

[3] Phil. Mag., 1, 321 (1926).

The main result of the research may at once be stated. It is found that Dr. Sethi's report requires to be modified and that even in the case of a doubly refracting powder, it is possible to obtain a genuine transmission provided that the particles are very fine, much finer in fact than is necessary in the case of an isotropic solid. The transmission of light however is only partial even for the most favourable wavelength in the spectrum, and is overlaid by a diffuse or irregular radiation. If the incident light be plane-polarised, the transmitted light is also polarised completely, while the diffuse radiation which is overlaid on it is mostly unpolarised. It would seem from this that the observations of Procopiu and Petrescu may have been vitiated by admixture of the light genuinely transmitted by the suspension with the light diffused by the particles. Theoretical considerations are set out below which indicate that this must be the case.

2. *Theory*.

The propagation of light through a heterogeneous medium has to be treated as a diffraction problem. We shall

[4] Ann. Sc. de L' Universite de Jasse, 17, 111 (1931).

[5] Ann. Sc. de L' Universite de Jasse, 17, 15 (1931).

here follow a method similar to that used by Sethi and Sogani, but elaborated further so as to obtain more precise results. We assume that a flat rectangular cell is filled with powder of a doubly refracting substance and a liquid mixture of suitable refractive index, and calculate the intensity and polarisation of the light transmitted through it.

Take X, Y, Z, a system of rectangular co-ordinates. Let the plane of the cell be (XY) perpendicular to the plane of the paper. Let the wave travel along Z—the direction of thickness of the cell. Let the direction of light vibration be along X. Now consider an element of wave-front encountering a single crystal whose optic axis lies along (θ, ϕ), where θ is the angle between the optic axis and Z (the wave-normal), and ϕ is the angle between the projection of the optic axis in the (XY) plane and the X co-ordinate. Now in the crystal the initial vibration becomes resolved along two perpendicular directions, one in the plane containing the optic axis and the wave-normal and the other in a perpendicular direction. Hence on emergence, if the incident vibration be $x=a \sin pt$ the extraordinary and ordinary vibrations will be

$$e=a \cos\phi \sin (pt+\delta_1)$$

$$o=a \sin \phi \sin (pt+\delta_2)$$

where δ_1 and δ_2 are the appropriate changes in phase suffered by the wave in its passage through the crystal. To find the effect after emergence, we resolve the vibrations again, parallel to X and Y. Resolving along Y, we have

$-a \cos \phi \sin \phi \sin (pt+\delta_1)$ due to the extraordinary vibration, and $+ a \cos \phi \sin \phi \sin (pt+\delta_2)$ due to the ordinary vibration. Along x, the resolved parts are respectively

$$a \cos^2\phi \sin (pt+\delta_1) \text{ and } a \sin^2\phi \sin (pt+\delta_2)$$

Now the wave is incident on a layer comprising a large number of crystals; if now n be the number per unit area, then, because the probability of a crystal lying between θ and $\theta+d\theta$, and ϕ and $\phi+d\phi$ is $\frac{\sin\theta.\,d\theta.d\phi}{4\pi}$, the component obtained after summing up over all the elements of the wave-front is proportional to

$$Y=-\frac{na}{4\pi}\int_{0}^{2\pi}\int_{0}^{\pi}\cos\phi\sin\phi.\,d\phi.\,\sin(pt+\delta_1)\sin\theta.\,d\theta$$

$$+\frac{na}{4\pi}\int^{2\pi}\int^{\pi}\cos\phi\sin\phi\,d\phi\sin(pt+\delta_2)\sin\theta.d\theta.$$

Now θ and ϕ are independent of one another, and δ_1 and δ_2 depend only on θ and not on ϕ. Therefore, the integrals vanish, *i.e.*,

$$Y=0$$

This shows, for a random orientation of the crystals the transmitted light, if any, will not be depolarised. To calculate the x component and from that, the intensity of the transmitted light, we picture the particles to be spherical and the spheres to be arrayed more or less regularly touching one another, the interspace being filled with the liquid mixture introduced. Naturally therefore part of the wave travels wholly through the fluid, and part through varying depths of the crystal. If r is the radius of the sphere, the part of area occupied wholly by the fluid is $\frac{4r^2-\pi r^2}{4r^2}=1-\frac{\pi}{4}$, and the part through solid is $\frac{\pi}{4}$, this then represents the partition of area between the fluid and the solid. Let μ, μ_0, μ_e respectively stand for the refractive index of the fluid, of the ordinary vibration and of the extraordinary vibration; also we suppose $\mu_e>\mu_0>\mu$. We write down the vibration issuing from the liquid at the other end of the layer considered, as $a\sin pt$.

Now as different elements of the wave will travel different thicknesses of the crystal, we take ψ and χ—a system of spherical polar co-ordinates within the crystal ; then for the part of the wave incident on the crystal at (ψ, χ) the retardation of the ordinary vibration will be

$$\frac{2\pi}{\lambda}\left[2r\cos\psi(\mu_o-\mu)\right]=\frac{4\pi r}{\lambda}(\mu_o-\mu)\cos\psi$$

where λ is the wave-length of light considered.

The extraordinary vibration suffers a further change in phase depending on the angle between the wave-normal and the optic axis (θ,ϕ) and this is

$$\frac{4\pi r}{\lambda}(\mu_e-\mu_o)\cos\psi.\ \sin^2\theta.$$

Also, the fraction of area traversed by the wave at (ψ,χ) is

$$\frac{\sin\psi.\ \cos\psi d\psi.d\chi}{\pi}$$

Hence for the vibration of the emergent light from both the crystal and the liquid, we get (omitting a or putting a equal to unity),

$$\left(1-\frac{\pi}{4}\right)\sin pt+\frac{\pi}{4}\int\sin^2\phi\sin\left[pt-\frac{4\pi r}{\lambda}(\mu_o-\mu)\cos\psi\right]\frac{\sin\theta.d\theta.d\phi}{4\pi}$$

$$\times\frac{\sin\psi\cos\psi\, d\psi\, d\chi}{\pi}+\frac{\pi}{4}\int\cos^2\phi\ \sin\left[pt-\frac{4\pi r}{\lambda}(\mu_o-\mu)\cos\psi-\frac{4\pi r}{\lambda}\right.$$

$$\left.(\mu_e-\mu_o)\sin^2\theta\cos\psi\right]\times\frac{\sin\theta.d\theta.d\phi}{4\pi}.\ \frac{\sin\psi.\ \cos\psi.\ d\psi.d\chi}{\pi}.$$

the limits of the integral being

θ	between	0	and	π
ϕ	,,	,,	,,	2π
ψ	,,	,,	,,	$\pi/2$
χ	,,	,,	,,	2π

Now put $\frac{4\pi r}{\lambda}(\mu_o-\mu)=\kappa.$

and $\frac{4\pi r}{\lambda}(\mu_e-\mu_o)=\tau$

It may be shown on simplifying and retaining up to the second order (regarding κ and τ as small quantities of the first order) and integrating, that the vibration is

$$\left(1-\frac{\pi\kappa^2}{16}-\frac{\pi\tau^2}{60}-\frac{\pi\kappa\tau}{24}\right)\sin pt-\frac{\pi}{6}\left(\kappa+\frac{\tau}{3}\right)\cos pt.$$

Hence the intensity is equal to

$$1-\frac{\pi\kappa^2}{8}-\frac{\pi\tau^2}{30}-\frac{\pi\kappa\tau}{12}+\frac{\pi^2\kappa^2}{36}+\frac{\pi^2.\tau^2}{36.9}+\frac{\pi^2}{36}.\frac{2\kappa\tau}{3}$$

Hence the average loss in intensity or absorption per layer is

$$\kappa^2\left(\frac{\pi}{8}-\frac{\pi^2}{36}\right)+\tau^2\left(\frac{\pi}{30}-\frac{\pi^2}{324}\right)+\kappa\tau\left(\frac{\pi}{12}-\frac{\pi^2}{54}\right)=a\text{ (say).}$$

Hence if I is the intensity of light encountering the xth layer,

$$dI=-a\,I.\,dx$$

$$\text{and } I=I_0\,e^{-aX}$$

where

I_0=intensity of the incident light ;

I=intensity of light after it has travelled X layers of the crystals.

Substituting for a and writing

$2r=d$=the diameter of the particle ;

$X\times d$=the total thickness$=t$;

X=total number of layers.

we have

$$I=I_o\, e^{\frac{-4\pi^2}{\lambda^2}\left[(\mu_o-\mu)^2\left(\frac{\pi}{8}-\frac{\pi^2}{36}\right)+(\mu_e-\mu_o)^2\left(\frac{\pi}{30}-\frac{\pi^2}{324}\right)+(\mu_e-\mu_o)(\mu_o-\mu)\times 1\left(\frac{\pi}{12}-\frac{\pi^2}{54}\right)\right]t.d.} \qquad \ldots \quad (A)$$

The particular case of a non-crystalline powder is obtained by putting $\mu_e=\mu_0=\mu'$ (solid) we obtain

$$I=I_o \exp. -\frac{4\pi^2}{\lambda^2}\, t.d.\, (\mu'-\mu)^2\left(\frac{\pi}{8}-\frac{\pi^2}{36}\right) \qquad \ldots \quad (B)$$

a formula very similar to that obtained and used by Sogani[6] in his experiment on "the optical properties of chromatic emulsions" and by Sethi[7] on powdered glass. By comparing the formulae (A) and (B) we find that the powder of an isotropic substance can be perfectly transparent for the particular wave-length for which the liquid-mixture and the solid have the same refractive index; but then the maximum transparency of a doubly refracting solid is limited by the intrinsic difference between the two refractive indices μ_e and μ_0 peculiar to the crystal. The formula in fact clearly indicates the increased absorption for the powder of a doubly refracting solid; in fact, unless particles are taken sufficiently fine to compensate for the additional factors contributing to the absorption, there will be no appreciable transmission, but only a diffuse radiation through the suspension.

3. *Some Experimental Results.*

The difference between the transmitting powers of the crystalline and non-crystalline powders was strikingly shown by fused quartz and crystalline quartz; whereas the former on immersion in a suitable liquid mixture showed very clear transmission with comparatively large particles and considerable thickness of the containing cell, the latter showed some transmission only when the particles were fine and the thickness of the cell rather small.

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[6] *Loc. cit.*

[7] *Loc. cit.*

The following observations were made with the powder of crystalline quartz immersed in a liquid mixture of benzene and carbon disulphide. It was first tested whether there is any depolarisation of the regularly transmitted beam. The refractive index of the liquid was adjusted so that the cell was transparent for the green region near 5461 line of mercury arc. A Zeiss green filter was placed in front of the mercury arc and the issuing green light was quenched by two crossed nicols. When the cell containing the heterogeneous medium was placed between the two nicols, no restoration of light (the image of the source) was visible. Of course, the restoration or the extinction could not be observed against a dark background as there always remained some diffused scattered light, which however did not change in intensity as the analyser was rotated. Hence it was concluded that the scattered light was indeed depolarised, but the regularly transmitted beam was not.

To measure the intensity of the transmitted light, a Hilger Nutting Spectrophotometer was used. The following table gives the results of experiment as well as the values of intensity to be expected according to the formula presented above. The thickness of the medium was $9 \cdot 5 \times 10^{-2}$ cm.

TABLE.

Wave-length $\times 10^7$ cm.	Intensity (Experiment).	Intensity (Theory).
656	·0151	·0101
589	·0199	·0128
546	·0767	·0907
486	·0878	·0672

Under the microscope, the particles were not of uniform size, the size varying from 2 to 5×10^{-4} cm. The greater number, however, showed a diameter of about $2{\cdot}7\times10^{-4}$ cm. actually used in the above computations. Since benzene and CS_2 especially show a rather large variation of refractive index with temperature, care was taken to ensure that both the refractive index and the intensity of light are measured at nearly the same temperature.

In conclusion, I tender my grateful thanks to Prof. Sir C. V. Raman, Kt., who suggested the problem and also guided me throughout the work; my thanks are also due to Prof. Dr. P. C. Mitter of the Chemistry department for his very kindly allowing me the use of his Pulfrich Refractometer.

Magnetic Birefringence in Solutions of Sodium Chlorate and Sodium Bromate

By

S. W. CHINCHALKAR.

(*Received for publication, 6th July, 1932.*)

ABSTRACT.

Sodium chlorate and sodium bromate in aqueous solutions are found to exhibit a feeble magnetic birefringence, negative in sign, and smaller in magnitude than that shown by nitrates, as was predicted by Krishnan from his observations on the magnetic anisotropy of potassium chlorate crystal. (Values are given in Table I.) The optical anisotropy of the chlorate ions, calculated from the magnetic birefringence and Krishnan's data, comes out of the same order of magnitude as is to be expected from the known birefringence of the crystal.

1. *Introduction.*

Apart from the great many organic compounds in which magnetic double refraction has been observed,[1] there are also a few inorganic substances [2] like water, nitric acid and nitrate and nitrite ions in solution which exhibit a magnetic birefringence. The sign of the birefringence is negative in water and positive in the other three mentioned. Raman and Krishnan [3] have shown a correlation between the magnetic birefringence in nitric acid and the optical and magnetic properties of the nitrate crystals. Recently, while measuring the magnetic susceptibilities of certain crystals in different directions, Krishnan[4] found that whereas in the nitrate crystals, the direction of maximum optical susceptibility nearly coincides with that of the minimum diamagnetic susceptibility, the reverse was seen to be the case for potassium chlorate crystals, the directions of maxima of the two coinciding. This indicated that the chlorate ions in solution should show a magnetic birefringence negative in sign, as opposed to the positive one shown by the nitrate ions.

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[1] See Landolt-Bornstein Tabellen, Zweiter Erganzungsband, p. 913.

[2] Ramanadham, Ind. Jour. Phys., 4, 109 (1929); Haque, C.R., *190*, 789 (1930).

[3] Raman and Krishnan, Proc. Roy. Soc., A, *115*, 549 (1927).

2. *Results.*

The author tested solutions of sodium chlorate and sodium bromate for magnetic birefringence using the same half-shade analyser to detect and measure the birefringence as he used for the aliphatic liquids,[5] the other experimental arrangement being also the same. The results are given in the table below, C_m being the relative value of magnetic birefringence on scale acetone $= +1·6$, *i. e.*, nitrobenzene $= +100$.

TABLE I.

Solute.	Concentration of the solution.	Concentration in gram. equivalents of the solute.	Density of solution.	Observed C_m of solution.	C_m after correcting for water.
Sodium chlorate.	0· 78gms. per c. c. solution.	$0·75 \times 10^{-2}$ gm. equivalent per c. c. solution.	1·42	$-0\ 36 \pm ·03$	$-0·26$
Sodium bromate.	0·31 gms. per c. c. solution.	$0·20 \times 10^{-2}$ gm. equivalent per c. c. solution.	1·22	$-0·26 \pm ·03$	$-0·11$

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[4] K. S. Krishnan, Phys. Rev., *38*, 833 (1931).

[5] S. W. Chinchalkar, Ind. Jour. Phys., *6*, 165 (1931).

The last column gives the magnetic birefringence due to chlorate or bromate ions after due correction is made for the water present, from the known concentration and density of the solution and assuming that the correction is proportional to the amount of water present. It is thus seen that the chlorate ions as expected from Krishnan's work, as also the bromate ions, show a negative magnetic birefringence. By comparing the values of C_m and the concentrations in equivalent weights, it can be seen that the bromate ions exhibit a stronger magnetic birefringence than the chlorate ions. It may be noted that the nitrate ions in a solution of the same equivalent concentration as that of sodium chlorate in the table, would exhibit a magnetic birefringence of the value $C_m = +0{\cdot}75$ nearly,[6] being thus in magnitude nearly three times that shown by the chlorate ions.

3. *Discussion.*

To compare the magnetic birefringence data for the chlorate ions with the magnetic and optical properties of the ions in the crystalline state, we take the case of potassium chlorate crystal cited by Krishnan. Potassium chlorate is a monoclinic crystal, but two of the principal refractive indices are very nearly equal, so that for practical purposes, it may be taken to be a uniaxial crystal. Zachariasen[7] has determined its crystal structure and finds that there are two molecules per unit cell so orientated that the planes containing the three oxygen atoms of the ClO^3 ions are parallel to one another. The direction perpendicular to the plane of the oxygen atoms is the axis of the approximate uniaxial crystal. It is also the direction of the minimum diamagnetic susceptibility, and the magnetic symmetry axis. The chlorine atom is not in the plane of the oxygen atoms. Since the induced magnetic moments in an ion are too small to affect the neighbouring ions in the crystal, the difference $(\chi_{11}-\chi_1)$ between the molar magnetic susceptibilities of the crystal along and perpendicular to the symmetry axis will be the sum of those for the individual ions. The optical moments are, however, known to be influenced by the neighbouring atoms and ions. Hence taking the magnetic susceptibility differences of the ions from the data for the crystal, and the experimental value of the magnetic birefringence, we can calculate on Langevin's theory the difference in the optical susceptibility of the chlorate ion in solution in the two directions, and compare it with the value found from the refractivities of the crystal. This is done below.

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[6] **Haque**, *loc. cit.*

[7] **Zachariasen**, *Zeit. f. Cryst.* *71*, 501 (1929).

According to Langevin's theory,[8] the formula for the Cotton-Mouton constant of magnetic birefringence can be put in the form

$$C_m=\frac{(n^2+2)^2\,\nu}{135 n\lambda k\mathrm{T}}\Big[(A-B)\;(A'-B')+(B-C)\;(B'-C')\;+(C-A)\,(C'-A')\Big] \qquad (i)$$

where A, B, C, are the optical moments induced in a molecule by a unit electric field of the incident light wave acting along the three mutually perpendicular directions of the optical ellipsoid of the molecule, A′, B′, C′, are the magnetic moments induced by a unit magnetic field along the same three directions, and ν is the number of molecules per c. c. In our case n would be the refractive index contributed by the chlorate ions, which can be calculated from the refractivity data for those ions. Also for these ions, if the axis of symmetry be taken to be the direction of A, then B′=C′, and

$$(A'-B')=\frac{\chi_{11}-\chi_1}{N} \qquad (ii)$$

where χ_{11} and χ_1 are the molar diamagnetic susceptibilities along and perpendicular to the axis of symmetry and N is the

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[8] Debye, Handbuch der Radiologie, Bd. VI, p. 769.

Avogadro number. Taking $(\chi_{11}-\chi_1)$ from Krishnan's data and the experimental value of C_m, and remembering that B=C, equation (*i*) gives the value of (A−B); thence an equation analogous to (*ii*) would give

$$N(A-B)=R_e-R_0 \qquad (iii)$$

where R_e and R_0 are the gram. molecular refractivities along and perpendicular to the axis. The value of (R_e-R_0) calculated in this way from equation (*i*) comes to −2·41±0·25. $(R-R_0)$ for $KClO_3$ crystal is −2·12 from the refractivity data given in the International Critical Tables,[9] and −2·97 from the data of Porter.[10] These are in fair agreement with the value obtained above, considering the divergence between the two crystal valves, and the relative error involved in the measurement of the constant of magnetic birefringence.

In conclusion, the author desires to express his grateful thanks to Prof. Sir C. V. Raman for his keen interest and suggestions.

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[9] Int. Crit. Tables. Vol. 1, p. 169.

[10] Quoted in Landolt Bornstein Tabellen, Zweiter Erganzungsband, p. 780.

25

Electronic Constitution of Some Simple and Complex Derivatives of Copper in Relation to their Magnetic Properties.

By

S. S. BHATNAGAR, BALWANT SINGH AND ABDUL GHANI.

(Received for publication, 25th July, 1932.)

ABSTRACT

1. The magnetic susceptibilities of 13 compounds of copper have been determined in solution and in the solid state.

2. It has been shown that the copper compound, in which the central metallic atom or ion contains completed sub-groups, possesses zero magnetic moment and is diamagnetic, whilst those in which the sub-groups are incompletely filled are paramagnetic.

In the formation of a co-ordination compound, according to Sidgwick (Jour. Chem. Soc., 1923, 123, 725), the central atom tends to assume the electronic configuration of the next higher inert gas, the co-ordinated atoms, groups or molecules being held by covalencies to the central nuclear atom. His view has been supported by Lowry (Jour. Soc. Chem. and Ind., 1923, 42, 316), Fowler (Discussion—Faraday Soc., "Electronic Theory of Valency," 1923) and Spiers (Jour. Soc. Chem. & Ind., 1923, 42, 534) and its importance has been revealed by Welo and Baudisch ("Nature," 1925, 116, 606) and Bose (Phil. Mag., 5, 1048, 1928).

Welo and Baudisch have brought into prominence the fact that the complex compounds whose 'effective atomic number,' is equal to that of the next higher inert gas exhibit diamagnetism as they form closed configurations like that of the latter. They also showed that complex compounds whose 'effective atomic number' falls short of or increases the inert gas configuration exhibit paramagnetism. Bose has gone a step forward and assumes that the magnetic moments of complex salts expressed in terms of Bohr's magneton are mostly proportional to the difference between their 'effective atomic number' and the atomic number of the next higher inert gas. Both these rules afford considerable support to the Sidgwick concepts of the structure of a co-ordination compound.

The magnetic properties of compounds, thus depend on the electronic configuration of the central atom. In general, atoms or ions which contain completed sub-groups possess zero, or very small magnetic moments and are diamagnetic, whilst those in which the sub-group is incompletely filled are paramagnetic.

Magnetic susceptibilities of some simple and complex derivatives of copper have been determined in this investigation with a view to elucidate their electronic constitution.

Experimental.

The copper compounds were prepared by the well-known methods.

1. The copper salts of fatty acids—copper acetate, copper propionate, copper butyrate, copper valerate, copper caproate—were prepared by neutralising the corresponding acids with copper carbonate.

2. The copper derivatives of β-diketones were obtained by the methods whose references are given separately in each case.

(*a*) Copper acetyl acetonate. Jour. Chem. Soc., 1914, **105**, 196.

(*b*) Copper benzoyl acetonate. Beilstein. VII, p. 769.

(*c*) Copper salt of aceto-acetic ester, Ber., 1898, **31**, 3153.

(*d*) Copper dimethyl glyoxime. "Collection," 1929, p. 151.

3. The complex derivatives of copper stabilised by ethylene diamine-bisethylene diammino-cupric nitrite, bisethylene diammino-cupric thiosulphate, bisethylene diammino-cupric hypophosphite were prepared according to the methods of Morgan and his co-workers (Jour. Chem. Soc., 1926, pp. 2018-2027 and 1927, p. 1264).

Tetra-kis-ethylene thio-carbamido cuprous nitrate was very kindly supplied by Prof. G. T. Morgan of the National Physical Laboratory, for which we are very highly grateful to him.

Magnetic susceptibilities of the copper salts, in solution were determined by the Quincke's method. Mass susceptibility of the solute was then calculated in each case by the application of Wiedemann's law (Pogg. Ann., 1865, 1, 126, and Jour. Amer. Chem. Soc., 1926, **48**, 847).

The results obtained in solution by the Quincke's method were further verified by finding out magnetic susceptibilities of the copper salts in the soild state [1] by the Guoy's method modified by Bhatnagar, Mathur and Kapur (Indian Jour. Phys., 1928, **3**, 56). From the magnetic susceptibility values of the copper salts, (p) Weiss magnetons were calculated in each case and the results are given in the following table.

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[1] Some of the observations in the soild state were made by Mr. P. L. Kapur for which we are thankful to him.

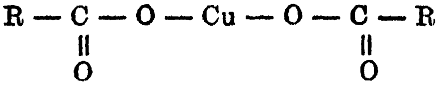
TABLE I.

Substance.	Mass Susceptibility. $\chi_m \times 10^6$.		Molecular Susceptibility. $\chi_M \times 10^6$.		Curie Constant. C_M.		Weiss Magneton p.		Mean. p.
	Quincke.	Guoy.	Quincke.	Guoy.	Quincke.	Guoy.	Quincke.	Guoy.	
Copper acetate	7·614	7·418	1520	1481	0·4605	0·4486	9·5	9·4	9·5
Copper propionate	6·054	6·704	1379	1527	0·4186	0 4626	9·1	9·6	9·4
Copper butyrate	5·624	6·046	1438	1546	0·4356	0·4793	9·3	9·7	9·5
Copper valerate	5·117	5·248	1359	1394	0·4118	0·4223	9·0	9·1	9·1
Copper caproate	4·905	5·089	1441	1495	0·4364	0·4529	9·3	9·5	9·4
Copper acetyl acetonate.	5·645	5·828	1477	1521	0·4482	0·4608	9·4	9·6	9·5
Copper benzoyl acetonate.	3·710	3·785	1431	1460	0·4357	0·4422	9·3	9·4	9·4
Copper salt of acetoacetic ester.	4·790	5·135	1540	1650	0·4668	0·4989	9·6	9·9	9·8
Copper dimethyl glyoxime.	4·912	5·577	1448	1676	0·4371	0·5078	9·8	10·0	9·7
Bisethylene diammino cupric nitrite.	5·837	6·198	1609	1700	0·4875	0·5174	9·8	10·1	9·9
Bisethylene diammino cupric thiosulphate.	5·295	6·413	1567	1605	0·4782	0·4863	9·7	9·8	9·8
Bisethylene diammino cupric hypophosphite.	5·115	5·212	1604	1685	0·4862	0·4955	9·8	9·9	9·9

Tetra-kisethylene thio-carbamido cuprous nitrate is found to be diamagnetic and its specific susceptibility determined by Wilson's balance is $-0{\cdot}55 \times 10^{-6}$.

Discussion.

According to Sidgwick ("The Electronic Theory of Valency," p. 254), the cupric derivatives of fatty acids are not chelate compounds but exist in a covalent form.



$$R-\underset{\underset{O}{\|}}{C}-O-Cu-O-\underset{\underset{O}{\|}}{C}-R$$

In this investigation these compounds are found to be paramagnetic and their (p) Weiss magneton values vary from 9 to 10 units. The magnetic moment of a molecule is due to spin moments of unpaired electrons. Thus the cupric ion in these compounds contains an incomplete sub-group and its electronic structure is represented as

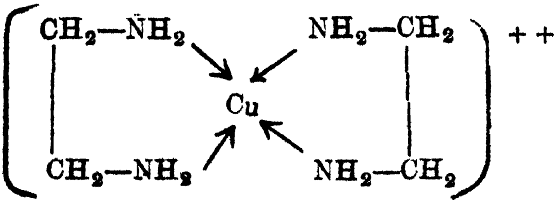
Cu^{++} 2, 224, 22445

The paramagnetism exhibited by these compounds is, therefore, due to the incomplete electronic M_{33} sub-group of the central metallic atom.

The influence of co-ordination upon magnetic moment has been studied experimentally by a number of workers, notably by Rosenbohm (Z. Physikal. Chem., 1919, 93, 693) and theoretical discussions have been given by Welo and Baudisch (*loc. cit.*). They trace a relation between the magnetic moment and the 'effective atomic number,' assuming that the co-ordinated groups are held by shared pairs of electrons.

The 'effective atomic number' in case of the cupric derivatives of β-diketones and dimethyl glyoxime is equal to $35 (29 + 1 \times 2 + 2 \times 2 = 35)$ as calculated according to Sidgwick's rules (The Electronic Theory of Valency, p. 163).

With ethylene diamine, copper forms a co-ordination complex having the following structure :

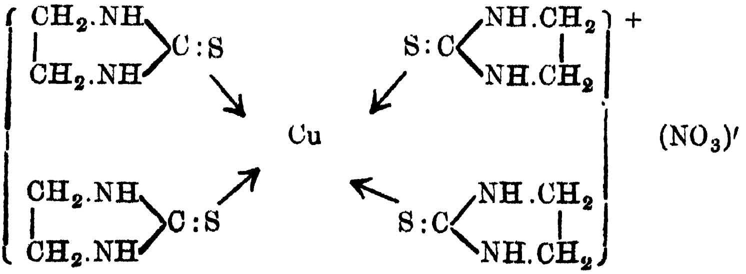


The central metallic atom is co-ordinated with two molecules of the base (ethylene diamine) and its effective atomic number is equal to $35(29+2\times4-2=35)$.

Thus the copper derivatives of β-diketones, dimethyl glyoxime and ethylene diamine are four-fold co-ordination compounds having 35 as the 'effective atomic number' of the central metallic atom. The electronic structure of the co-ordinated copper atom is represented as 2, 224, 22445, 224 which differs from the arrangement 2, 224, 22446, 224 for krypton, the next inert gas, in a shortage of one electron in the ninth (M_{33}) sub-group. According to Welo and Baudisch and Bose such compounds should exhibit paramagnetism.

In this investigation copper acetyl acetonate, copper benzoyl acetonate, copper salt of aceto-acetic ester, copper dimethyl glyoxime, bisethylene diammino cupric thiosulphate, bisethylene diammino cupric nitrite and bisethylene diammino cupric hypophosphite are all experimentally found to be paramagnetic in accordance with the theory. These observations, therefore, confirm the structure assigned to the copper complex compounds.

In tetrakisethylene thiocarbamido-cuprous nitrate, (Cu. 4 etu) NO_8, which may have the following structure :—



the cuprous ion is eight electrons short of the number required for the krypton structure, but by becoming co-ordinated with four molecular proportions of cyclic thio-base (ethylene thiocarbamide etu) it acquires these additional electrons. In other words its 'effective atomic number' calculated according to Sidgwick's rules would become equal to 36; because each of the ethylene thio-carbamide molecule adds two electrons and the $(NO_3)'$ radical attached to the complex by an electrevalent link, removes one electron thus leaving the total number of electrons associated with the central copper atom equal to 36 ($29 + 2 \times 4 - 1 = 36$).

The number of electrons associated with the central copper atom in the complex is thus the same as the number in the inert gas atom krypton, and presumably forms a closed configuration of the inert gas type, with a zero magnetic moment. It has been verified experimentally as the complex compound is found to be diamagnetic.

The influence of co-ordination upon magnetic moment in case of the complex compounds of copper studied in this investigation is summarised in the following table.

TABLE II.

Compound.	Co-ordination number.	Effective Atomic Number.	MAGNETIC MOMENT.	
			Weiss Magnetons.	Bohr Magnetons.
Copper acetyl acetonate ...	4	35	9·50	1·91
Copper benzoyl acetonate ...	4	35	9·35	1·88
Copper salt of aceto-acetic ester ...	4	35	9·75	1·96
Copper dimethyl glyoxime ...	4	35	9·65	1·94
Bisethylene diammino cupric thiosulphate	4	35	9·75	1·96
Bisethylene diammino cupric nitrite	4	35	9·90	1·99
Bisethylene diammino cupric hypophosphite	4	35	9·85	1·98
Tetrakisethylene thio-carbamido cuprous nitrate	4	36	0·0	0·0

The values of the magnetic moments in Bohr magnetons for the above compounds are in accordance with Bose's rule $(Z-Z' = n)$ where (Z) is the atomic number of the next inert gas, (Z') the effective atomic number of the co-ordinating atom and (n) the number of Bohr magnetons.

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Annual Report for 1931.

The following report on the activities of the Indian Association for the Cultivation of Science during the year 1931 is respectfully submitted to the Committee of Management.

PART I.

REPORT ON SCIENTIFIC INVESTIGATIONS.

1. The Raman Effect.
2. Magnetism and Magneto-optics.
3. X-ray Diffraction.
4. Cathode Luminescence.
5. List of Papers published in 1931.

PART II.

ADMINISTRATIVE REPORT.

6. Our Research Workers.
7. Lecture Arrangements.
8. Laboratory Equipment.
9. Workshop.
10. Library and Reading Room.
11. Financial Statement.
12. Acknowledgments.
13. Statement of Accounts for 1931.

PART I.

REPORT ON SCIENTIFIC INVESTIGATIONS.

1. *The Raman Effect.*

Subsequent to last year's report, various aspects of the subject have been under investigation and certain new branches were opened. Bhagavantam developed a special technique for the study of the Raman effect in gases maintained at pressures ranging up to 50 atmospheres. Special precautions, taken to prevent the parasitic light reflected from the walls of the container vessel, resulted in a number of important and new features being revealed in the spectra of most common gases. Using this method, he was able to analyse the rotation spectra of hydrogen, nitrogen and oxygen. Pressure was found to have a marked effect on the sharpness of the individual rotation lines. In some cases, they showed a tendency to broaden out and merge into each other above a certain critical pressure which could be computed from considerations of the frequency of collisions as derived from the kinetic theory of gases. Preliminary estimates of the absolute intensities and polarisation characters of the various Raman lines in simple molecules in the gaseous state have also been made. A comparison of the results with the existing theories of Raman scattering showed that, while the general ideas regarding the origin of the vibrational and rotational scattering are essentially correct, there is however a serious discrepancy between the predicted and observed intensities of the rotational scattering. This led to the very important and fundamental consequence that light quantum has an intrinsic angular momentum of one Bohr unit. In order to test the consequences of this idea, the technique of photographing the light scattered by gases entirely free from parasitic illumination was considerably improved and spectrophotometric methods of determining its state of polarisation developed.

In a paper published in the Indian Journal of Physics, the results have been described in detail. In two other papers, Bhagavantam has considered the possibility of explaining several features in the Raman scattering by gases from a purely classical standpoint and has arrived at results which are in good agreement with those derived from quantum theories.

In continuation of his researches on the scattering of light by crystal powders already reported in the year 1930, Dr. Krishnamurti extended the studies to a number of other inorganic crystals. He has also studied various physico-chemical phenomena such as hydrate formation and hydrolytic dissociation by the help of the Raman effect. With a view to obtain the complete Raman spectra of liquids in an unambiguous manner, Dr. Krishnamurti developed a special filter technique and with this method he investigated a few organic substances such as pyridine, acetic acid, benzene, cyclohexane and octane. In these compounds, he was able to obtain many new frequencies, hitherto unrecorded, and thereby establish a more or less complete correlation between the Raman effect data and infra-red absorption maxima.

An important line of work started by Mr. Sirkar in this laboratory was the accurate measurement of the intensities of the Raman lines in liquids and was referred to in the report for the previous year. During the year under report, he extended the investigations to other cases and compared the intensity of the Raman lines with those of the incident exciting mercury lines. Supporting his previons work, he found that there were marked deviations from the Rayleigh fourth power law, the intensities of the Raman lines in the ultra-violet region increasing more rapidly than is indicated by the said law. He also studied the ratio of the intensities of the Stokes and anti Stokes Raman lines in carbon tetrachloride and showed that the ratio conformed very exactly to the theoretical expressions given by Placzek.

Dr. Venkateswaran studied the Raman effect in a number of substances falling into well defined chemical groups such as organic sulphides, inorganic halides, etc., and discussed the results in relation to the structures of these compounds.

A particularly complete analysis of the Raman spectrum of an interesting substance, *viz.*, formic acid was made by Mr. Parthasarathy.

2. *Magnetism.*

Mr. Chinchalkar studied the magnetic birefringence in aliphatic liquids by a sensitive half shade analyser. The precise values obtained enabled him to draw some interesting conclusions and supplement those drawn by Mr. Ramanadham earlier in this laboratory. The magnetic birefringence in carbon disulphide, though negative in sign like the other aliphatics, is known to be much larger in magnitude, being comparable with that of benzene. But calculations showed that the large value is due to its strong optical anisotropy, its magnetic anisotropy being much smaller than that of benzene and of the same order as that of other aliphatics. A comparison of magnetic anisotropies of organic molecules with their optical anisotropies also enabled him to find an interesting relation between these properties and the chemical structure.

The most significant investigation on the magnetic birefringence made in the laboratory during the year under report was the discovery of a new type of magnetic birefringence. So far, all the substances showing this phenomenon were known to belong to the diamagnetic class. Mr. Chinchalkar investigated the magnetic birefringence in the solutions of certain paramagnetic salts and found that salts of cerium, praseo-dymium, didymium and erbium showed a negative birefringence comparable with that in organic liquids. Gadolinium nitrate did not show an appreciable effect though it is strongly paramagnetic. It is interesting to find that the paramagnetism of the gadolinium ions is due entirely to the spin of the electrons, while that of the others is partly due to the orbital motion of the electrons, indicating that an orbital contribution is necessary for the appearance of a paramagnetic birefringence. Tentative calculations of the magnetic birefringence to be expected on Langevin's theory from cerium ions in solution, assuming that the ions have the same optical anisotropy as xenon atoms, give values which are of the same order as the experimental ones.

Using a modified form of Quincke's capillary ascension method, Mr. S. P. Ranganadham studied the magnetic susceptibilities of liquid mixtures. He found that they exhibited small deviations from the linear law which are of the same order as the corresponding deviations in densities of these mixtures.

Another important line of work started by Mr. Pillai was the investigation of the Faraday effect in paramagnetic solutions at different temperatures. He found that while for most of the solutions studied, the effect was nearly inversely proportional to the absolute temperature, in a few cases it was unaffected by changes in temperature and in one case, *viz.*, that of ferric salts, it even increased with increasing temperature.

3. *X-ray Diffraction.*

Mr. S. Ranganathan studied the X-ray diffraction patterns of a number of gall-stones and arrived at some interesting conclusions. In all the varieties of stones examined, he found that the constituents were deposited in a crystalline state although there were minor variations as to the size of the crystalline particles in different stones. A comparison is made of the patterns obtained in various gall-stones with the diffraction patterns for pure uric acid and cholesterol, the substances which usually constitute the above stones.

4. *Cathode Luminescence.*

In a study of the Raman effect in a large variety of diamonds, Mr. Bhagavantam recorded a strong band accompanied by a continuous spectrum in the scattered light and identified these radiations as fluorescence which is typical of diamonds. In order to test this idea, Mr. John examined the spectrum emitted by diamonds under the bombardment of cathode rays and obtained some very interesting results. The band and the continuous radiation appeared in exactly the same position as in the above case. This investigation opens up a new field of research intimately connected with crystal structure and may be extended to a number of other solids.

5. *List of Papers published during the year 1931.*

Indian Journal of Physics,

Vol. VI, Part I.

1. A Study of the Raman Effect in Amorphous Solids—By S. Bhagavantam.
2. Raman Spectra of Inorganic Crystals: Part III—By P. Krishnamurti.
3. Raman Spectra of Some Organic Sulphides: Part I—By S. Venkateswaran.

Vol. VI, Part II.

4. The Influence of Exciting Frequency on the Intensities of Lines in Raman Spectra—By S. C. Sirkar.

Vol. VI, Part III.

5. Magnetic Double Refraction in Aliphatic Liquids—By S. W. Chinchalkar.

Vol. VI, Part IV.

6. The Molecular Scattering of Light: Nobel Lecture—By Sir C. V. Raman.

7. The Raman Spectra of Some Inorganic Halides—By S. Venkateswaran.

8. The Raman Spectrum of Formic Acid—By S. Parthasarathy.

9. On the Relative Intensities of Stokes and Anti-Stokes Lines in the Raman Spectrum—By S. C. Sirkar.

10. Cathode Luminescence of Diamond—By M. V. John.

11. Raman Spectra of Some Organic Crystals and Solutions—By P. Krishnamurti.

12. Raman Effect in Gases: I. Some Experimental Results—By S. Bhagavantam.

13. Raman Effect in Gases: II. Some Theoretical Considerations—By S. Bhagavantam.

14. Study of Hydrolytic Dissociation by Raman Effect—By P. Krishnamurti.

15. Experimental Proof of the Spin of the Photon—By Sir C. V. Raman and S. Bhagavantam.

Vol. VI, Part V.

16. The Complete Raman Spectrum in relation to Infra-red absorption. Part I, Pyridine and Acetic Acid—by P. Krishnamurti.

17. Reversal of Circular Polarisation in Raman Scattering—By S. Bhagavantam.

18. Raman Effect and Formation of Hydrates in Solution—By P. Krishnamurti.

19. Magnetic Susceptibilities of Liquid Mixtures—By S. P. Ranganadham.

20. X-Ray Diffraction Studies in Calculi—By S. Ranganathan.

21. A Note on the Scattering of Light in Urines—By S. Ranganathan.

Vol. VI, Part VI.

22. The Complete Raman Spectrum in relation to Infra-red Absorption. Part II, Benzene, Cyclohexane and Octane—By P. Krishnamurti.

23. Raman Effect in Gases. III. Comparison of Theory and Experiment—By S. Bhagavantam.

24. Magnetic Birefringence and Molecular Anisotropy—By S. W. Chinchalkar.

25. Thermal Variation of Faraday Rotation—By P. K. Pillai.

26. A New Type of Magnetic Birefringence—By S. W. Chinchalkar.

27. Raman Spectra of the Simpler Hydrocarbons—By S. Bhagavantam.

Zeitschrift fur Kristallographie, Band 77, 1931.

28. Raman Effect in Calcite and Aragonite—By S. Bhagavantam.

Nature, 1931.

29. Raman Spectrum of Hydrogen Peroxide—by S. Venkateswaran.

30 Raman Spectra of Gases—By S. Bhagavantam.

31. Diamagnetism of Liquid Mixtures—By S. P. Ranganadham.

32. Polarisation of Raman Scattering by Hydrogen Gas—By S. Bhagavantam.

33. Evidence for the Spin of the Photon from Light-scattering—By Sir C. V. Raman and S. Bhagavantam.

34. Effect of Pressure on Raman Spectra—By S. Bhagavantam.

35. Intensity of Raman Scattering in Gases—By S. Bhagavantam.

36. Experimental Demonstration of Spin of Light—By Sir C. V. Raman and S. Bhagavantam.

37. Angular Momentum of Light—By Sir C. V. Raman.

38. India's Debt to Faraday—By Sir C. V. Raman.

39. Doppler Effect in Light-scattering—By Sir C. V. Raman.

40. Raman Spectra of Liquid Mixtures—By P. Krishnamurti.

41. Spin of Light Quanta—By Sir C. V. Raman and S. Bhagavantam.

42. A New Type of Magnetic Birefringence—By Sir C. V. Raman and S. W. Chinchalkar.

43. Atoms and Moleculess as Fitzgerald Oscillators—By By Sir C. V. Raman.

44. Light-scattering in Liquids—By S. Vankateswaran.

PART II.

ADMINISTRATIVE REPORT.

6. *Our Research Workers.*

Facilities for research work in our laboratory were given during the year 1931 to 35 research workers belonging to different Provinces. The King Edward Memorial Society of Nagpur has deputed a research scholar at their expense to work in the laboratory of this Association.

7. *Lecture Arrangements.*

Regular courses of lectures in physics and chemistry for the benefit of students were delivered at the Association with the aid of our apparatus and demonstrators.

8. *Laboratory Equipments.*

The following additions have been made during the year to our stock of apparatus :—

1. One Park Royal Ammeter 0-10.
2. One High Illumination Spectrograph No. 105-5987.
3. One Leitz Epidiascope.
4. One Photo-Micrographic Camera.
5. One Table Polishing Machine with 220-volt Motor and three discs.
6. One Universal Colorimeter complete with cups and Microcups plungers and Nephelometer. Attachment lamp and Resistance.
7. One Polarising microscope with objectives I and III Eye-piece, etc.
8. One Micro-Camera Attachment.
9. One Arc Lamp with condensing lens.
10. Two fixed Resistances.
11. One Transformer 110 Volts and 22 V. A. C. to 6 V. 5 Amp. with Ammeter.
12. One Aplanatic Nonspherical lens, C. Zeiss.
13. Three Pointolite Mercury Arc Lamps.
14. One Screen for Projection.
15. One Dozen Pure Carbon, Adam Hilger } with Hilger
16. One Packet 2 gramms R. U. Powder } certificates.
17. Three Thick Quartz tubes.
18. One Quartz Burner.
19. Three Plane parallel glass plates, Zeiss.
20. Two Photometer Screens Platinum Sputtered.

21. 6 yds. Thick Tungsten Wire.
22. 1000 C.P. Pointolite.
23. One 8″ Condenser.

9. *Workshop.*

The following apparatus were manufactured during the year by the mechanics in the Workshop of the Association :—

1. One High-pressure steel apparatus for investigation of Raman Effect in gases.
2. Four Electrical Heaters.
3. Two Hartmann Diaphragms.
4. Two Wedges for Spectroscope slits.
5. Union Nuts for gas cylinders.
6. One Left-handed screw adapter.
7. Four brass clamps and stands for magnetic work.
8. Two lead slits for X-ray work.
9. A few accessories of steel sockets, etc., for steel protecting tube for high-pressure gas work.
10. Fittings of black glass as background for high-pressure work.
11. Fitting up of pressure gauges for high-pressure gas work.
12. One Liquid stirring apparatus.
13. Apparatus for investigation on mechanical birefringence in liquids.
14. Four adjustable metallic plate-holders for grating, etc.
15. One stout steel cross tube for high-pressure gas work.
16. Modification of safety valves for Liquid-air Machine.
17. Brass apparatus, Rayleigh's Refractometer.
18. One Goniometer.

Besides the above apparatus, numerous repairs and fittings for Laboratory were executed during the year under report.

10. *Library and Reading Room.*

The following publications were subscribed for as usual:—

1. Scientific American.
2. Nature.
3. Science Abstracts, A and B.
4. American Journal of Science.
5. Philosophical Magazine.
6. Astrophysical Journal.
7. Chemical News.
8. Proceedings of the Royal Society, A.
9. Proceedings of the Royal Institution of Great Britain.
10. Transactions of the Royal Society, A.
11. Physical Review.
12. Physikalische Berichte.
13. Zeitschrift fur Physik.
14. Annalen der Physik.
15. Physikalische Zeitschrift.
16. Journal of the American Chemical Society.
17. Journal of Physical Chemistry.
18. Proceedings of the National Academy of Sciences, Washington.
19. Zeitschrift fur Kristallographie, A and B.
20. Zeitschrift fur Physikalische Chemie.
21. Annales de Physique.
22. Comptes Rendus.
23. Chemical Abstracts.
24. Revue de Optique.
25. Science Progress.
26. Naturwissenschaften.
27. Journal of the Chemical Society of London and British Chemical Abstracts, A.
28. Transactions of the Faraday Society.
29. Zeitschrift fur Astrophysik.

We have to acknowledge with thanks the presentation of Journals and periodicals in exchange for our Proceedings from the following Societies and Institutions :—

1. The Smithsonian Institution.
2. Cambridge Philosophical Society.
3. Physico-Mathematical Society, Tokyo, Japan.
4. Manchester Literary and Philosophical Society.
5. American Philosophical Society.
6. University of Illinois.
7. Academie der Wissenschaften, Leipzig.
8. Franklin Institute.
9. South African Association for the Advancement of Science.
10. The Prussian Academy of Science, Berlin.
11. University of Philadelphia.
12. The Physical Society of France.
13. Bureau of Standards, Washington.
14. University of Iowa.
15. University of Calcutta.
16. Calcutta Mathematical Society.
17. Indian Chemical Society.
18. Reale Academia Nazionale Die Lincei, Rome.
19. Society de Physique et D'Historie-Naturelle, Geneve.
20. Bayerischen Academie der Wissenschaften, Munchen.
21. Der Gesselschaft de Wissenschaften, Gottingen.
22. University of Allahabad.
23. Imperial Agricultural Institute, Pusa.
24. Asiatic Society of Bengal.
25. Indian Institute of Science, Bangalore.
26. The Geological Survey of India.
27. Indian Mathematical Society (Presentation from Prof. Sir C. V. Raman).
28. Academy of Sciences, Cracow.
29. University of Brazil.

30. University de la Bruno.
31. Academy of Sciences, Leningrad, Russia.
32. University of Durham.
33. Royal Academy of Sciences, Amsterdam.
34. Imperial Academy, Tokyo, Japan.
35. De La Facultad de Sciences, La Plata.
36. Royal Meteorological Society, London.
37. University of Frankfurt-a-main.
38. Royal Dublin Society.
39. Tohoku Imperial University.
40. Institute of Physical and Chemical Research, Japan.
41. Royal Academy of Sciences, Copenhagen.
42. Kodaikanal Observatory.
43. College of Science, Kyoto, Japan.
44. National Research Council, Japan.
45. Academy of Sciences, Vienna, Austria.
46. Proceedings of the Royal Society " B," London. (Presentation from Prof. Sir C. V. Raman.)
47. Transactions of the Royal Society " B," London. (Presentation from Prof. Sir C. V. Raman.)
48. Societe Chimique, Zagreb, Yougoslave.
49. Hungary University (Szeged).
50. Ungarische Akademie, Budapest.
51. American Chemical Society (Industrial and Engineering Chemistry).
52. Della Societa Italiana Di Fisica.
53. Societe De Chimie-Physique, Paris.
54. Mathematikai es Physikai Akademia, Budapest.
55. National Physical Laboratory of London.
56. Nederlandsch Tijdschrift Voor Naturkunde.
57. Physical Society of London.
58. Comite de Revue Generale des Sciences.
59. Editor of 'Physique Theorique.'
60. University of Upsala.
61. University of California.

62. Wissenschaftliche Veroffentlichungen aus dem Siemens Konzern.
63. Societe Polanaise de Physique, Warszawa.
64. Societe Vaudoise des Sciences Naturelles, Lausanne.
65. United States Department of Agriculture.
66. The Editor of Terrestrial Magnetism and Atmospheric Electricity.
67. De L'Institute Pasteur, Paris.
68. Swiss Physical Society.
69. Canada Geological Survey.
70. Society Polonaise des Naturalistes Kopernik.
71. Royal Canadian Institute.
72. Deutschen Naturwissenschaftlich-Medizinischen Verein fur Bohmen " Lotos " (Prag).

The following books were purchased during 1931 :—

1. Astrophysik, by S. Rosseland.
2. The New Conceptions of Matter, C. G. Darwin.
3. Studies in Optics, A. A, Michelson.
4. Spectra, R. C. Johnson and C. W. Richardson.
5. Elements of Thermodynamics, by Fernald.
6. Recent Advances in Analytical Chemistry, Vols. I and II, C. A. Mitchell.
7. Molecular Rearrangements, C. W. Porter.
8. Spectroscopy, Vols. I, II & III, E. C. C. Baly.
9. A Comprehensive Treatise on Inorganic and Theoretical Chemistry, Vol. XI, J. W. Mellor.
10. The Mechanism of Homogeneous Organic Reactions from the Physical-Chemical Standpoint, Francis Owen Rice.
11. Donnees Neumeriques de Spectroscopie, Vol. VII.
12. Landolt-Bornstein Physikalisch-Chemische Tabellen. Part I, 1931. 2nd Extra Band, 2nd Series 1931.
13. Handbuch der Experimental Physik, Band II, 3 Teil, Band IV, Teil I, Band XXV, 2 Teil.

14. Handbuch der Spectroscopie, Kayser.
15. Gmelins Handbuch der Anorganischen Chemie, 8 Auflage Sys. No. 59 and Teil B. 4.
16. Handbuch der Experimental Physik, Additional Band I, 1931, W. Weizel.
17. Der Smekal-Raman Effect, K.W.F. Kohlrausch.
18. Encyklopadie der Mathematischen Wissenchaften—Band III, No. 10.
19. International Critical Tables, Vol. VII, Index Vols. I to VII.
20. Report of the British Association for the Advancement of Science, 1930.
21. Tables Annuelles de Constants de Donnees Numeriques, Vols. I and V. 1930.

11. *Financial Statement.*

Government Securities in Bank—31st December, 1931.

	Rs.	AS.	P.
General Fund	1,87,800	0	0
Ripon Prof. Fund	17,000	0	0
Victoria Prof. Fund	1,000	0	0
Cooch-Behar Prof. Fund	21,500	0	0
Hare Prof. Fund	1,000	0	0
Nikunja G. Prize Fund	500	0	0
Jotindra Ch. Prize Fund	600	0	0
Joykissen Medal Fund	9,000	0	0
Woodburn Medal Fund	500	0	0
Dr. Sircar Research Medal Fund	3,000	0	0
Floating Balance in the Bank	1,18,475	3	1
Cash Balance in the Office	524	7	3

Government Securities in Bank—31st December, 1930.

	Rs.	As.	P.
General Fund	1,87,800	0	0
Ripon Prof. Fund	17,000	0	0
Victoria Prof. Fund	1,000	0	0
Cooch-Behar Prof. Fund	21,500	0	0
Hare Prof. Fund	1,000	0	0
Nikunja G. Prize Fund	500	0	0
Jotindra Ch. Prize Fund	600	0	0
Joykissen Medal Fund	9,000	0	0
Woodburn Medal Fund	500	0	0
Dr. Sircar Research Medal Fund	3,000	0	0
Floating Balance in the Bank	1,13,215	2	8
Cash Balance in the Office	1,520	12	0

12. *Acknowledgments.*

The thanks of the Association are due to the Honorary Engineer Babu Bhabadeb Chatterjee, the Honorary Legal advisers, Babu Jatindra Nath Basu, Babu Nirmal Chunder Chunder and Babu Jyotish Chandra Pal, to the Honorary Secretary Sir Venkata Raman and to the Honorary Assistant Secretaries Dr. P. Krishnamurti and Babu Ashutosh Dey for their gratuitous services.

Statement of Accounts for 1931.

Receipts.

		Rs.	As.	P.
Subscriptions		232	0	0
Donations		200	0	0
Rent from shops		4,332	0	0
Miscellaneous Receipts		2,021	4	6
Dr. Sircar Memorial Fund		705	0	0
Building Fund		250	0	0
Government of India Grant		20,000	0	0
Sale of Publications		3,122	4	8
Advertisement		275	0	0
Interest Account,	General Fund	9,784	12	0
„	Ripon P. Fund	575	0	0
„	Nikunja G. Prize Fund	17	8	0
„	Jatindra Ch. Prize Fund	21	0	0
„	Woodburn Medal Fund	17	8	0
„	Dr. Sircar Medal Fund	105	0	0
„	Victoria Prof. Fund	35	0	0
„	Cooch-Behar Prof. Fund	752	8	0
„	Hare Prof. Fund	35	0	0
„	Joykissen Medal Fund	315	0	0
Suspense Account		193	14	0
Provident Fund		884	9	10
Old Material Sale		50	8	0
Post Office Savings Bank withdrawn		520	0	0
Opening Balance on 1st January, 1931—				
At Imperial Bank		1,13,215	2	8
At Office		1,520	12	0
	TOTAL	1,59,180	11	8

Examined and Found Correct.

SAHA & MAZUMDER,

Government Certified Auditors.

The Year Ended 31st December, 1931.

Payments.

	Rs.	As.	P.
Commission a/c General Fund	28	12	0
„ Ripon Prof. Fund ...	1	6	0
„ Nikunja G. P. Fund ...	0	3	0
Establishment Account ...	6,995	13	3
Municipal Tax	685	12	0
Electric Charges	3,201	11	6
Gas Charges	219	3	3
Building Repairs	876	2	9
Laboratory Charges	4,918	2	9
Workshop Charges	829	10	6
Postage and Telegram	1,425	9	6
Printing Charges	1,854	2	6
Miscellaneous Charges	2,438	0	6
Telephone Charges	239	1	6
Research Scholarship	6,075	0	0
Institute Contribution to Provident Fund ...	168	2	0
Scientific Instrument, General Fund ...	4,146	9	3
Library	3,305	1	3
Electric Accessories	352	4	0
Post Office Savings Bank Deposits ...	476	3	10
Furniture	992	2	0
Suspense	179	0	0
Provident Fund	248	0	0
Maharaja of Darbhanga Fund	525	0	0
Closing Balance on 31st December, 1931—			
At Imperial Bank ...	1,18,475	3	1
At Office	524	7	3
TOTAL	1,59,180	11	8

Balance Sheet.

Liabilities.

		Rs.	AS.	P.
General Fund		2,11,052	2	11
Investment Reserve Fund		1,16,094	0	0
Depreciation Reserve Fund,	Property	51,852	6	3
,, ,,	Instrument	55,495	7	8
,, ,,	Furniture	4,921	0	0
,, ,,	Library	18,550	12	4
Provident Fund		2,964	2	5
Victoria Prof. Fund		1,000	0	0
Ripon Prof. Fund		17,000	0	0
Hare Prof. Fund		1,000	0	0
Maharaja of Cooch-Behar Prof. Fund		21,500	0	0
Nikunja Garabini Prize Fund		500	0	0
Jatindra Chandra Prize Fund		600	0	0
Joykissen Medal Fund		9,000	0	0
Woodburn Medal Fund		500	0	0
Dr. Sircar Research Medal Fund		3,000	0	0
Dr. Sircar Memorial Fund		15,850	12	3
Vizianagram Fund		40	0	0
Building Fund		7,580	0	0
Maharaja of Darbhanga Fund		400	0	0
Viharilala Building Fund		1,00,000	0	0
Dr. Sircar Medal Fund, Interest		1,050	0	0
Nikunja Garabini Prize Fund, Interest		334	10	2
Ripon Prof. Fund, Interest		2,785	10	3
Woodburn Medal Fund, Interest		246	8	0
Jatindra Chandra Prize Fund, Interest		207	11	0
Joykissen Medal Fund, Interest		1,599	0	0
Victoria Prof. Fund ,,		140	0	0
Hare Prof. Fund ,,		140	0	0
Maharaja of Cooch-Behar Prof. Fund		3,010	0	0
Government of India Grant		366	12	9
	TOTAL	6,48,781	0	0

SAHA AND MAJUMDER,
Government Certified Auditors.

As at 31st December, 1931.

Assets.	Rs.	AS.	A.
Land and Old Building	31,680	11	9
Lecture Hall and Gallery	23,465	5	3
Vizianagram Laboratory	40,900	14	0
Observatory Room	3,320	9	9
Range of Shops (East)	2,516	10	9
Range of Shops (West)	2,308	5	0
Servants Quarters	1,024	0	0
Darwans' ,, ...	303	13	9
Scientific Instruments (K. K. Tagore Fund)	25,000	0	0
Scientific ,, (General Fund) ...	84,431	2	5
Botanical ,, ...	2,329	6	0
Workshop ,, ...	9,861	5	9
Tools and Implements	203	3	3
Library a/c	45,780	15	4
Furniture a/c	14,102	0	3
Suspense a/c	17	11	0
Government Securities 3½ per cent. G. Fund	1,87,800	0	0
,, Ripon Prof. Fund	13,000	0	0
,, Victoria Prof. Fund	1,000	0	0
,, Cooch-Behar Prof. Fund ...	21,500	0	0
,, Hare Prof. Fund	1,000	0	0
,, Nikunja G. P. Fund	500	0	0
,, Jatindra Ch. P. Fund ...	600	0	0
,, Joykissen M. Fund	9,000	0	0
,, Woodburn Medal Fund ...	500	0	0
,, Dr. Sircar Research Medal Fund ...	3,000	0	0
,, G. P. Notes 3 per cent. Ripon Prof. Fund ...	4,000	0	0
Balance at Post Office Savings Bank ...	635	3	5
Imperial Bank of India	1,18,475	3	1
Office	524	7	3
TOTAL ...	6,48,781	0	0

C. V. RAMAN,
Hony. Secretary.

Molecular Rotation in Liquids as Revealed by the Raman Effect.

By

S. P. RANGANADHAM.

(*Received for publication, 4th August, 1932.*)

ABSTRACT.

The depolarisation of the scattered light is spectroscopically determined for λ 4046 and 4358 radiations of the mercury arc, using successively narrow and wide slits for 14 different liquids. From these observations, the aggregate intensity of the rotation wing in relation to that of the pure Rayleigh scattering is deduced. A computation of this quantity is made on the assumption that the theory developed by Manneback for the rotational scattering by gases is applicable also to liquids. When modifications recently indicated by Raman and Bhagavantam are taken account of, good agreement is found between the observed and calculated intensities of the rotation scattering in a large number of non-associating liquids such as benzene. It is concluded that in such liquids, the molecules are more or less free to rotate. On the other hand, the results show that in highly viscous or associating liquids like salol or formic acid, the intensity of the rotation wing is far below the theoretically expected value and thus they suggest a large impedance to molecular rotation in such cases.

The last section is devoted to an experimental investigation of the intensity distribution in the rotation wing of benzene. The results show that there is a gradual falling off of intensity from a maximum at or very near the Rayleigh line itself. This is not in accordance with the view that a single molecule of benzene is the scattering unit and as such a tentative explanation, that groups of molecules having high moment of inertia are responsible for such a result, is suggested.

1. *Introduction.*

The diffuse wings that appear on eicher side of the Rayleigh line in the light scattered by certain liquids were recognised and explained by Raman and Krishnan [1] as due to exchanges of rotational energy between the molecules and the impinging light quanta. They found that the effect was very marked in certain substances like benzene and carbon disulphide while it was hardly noticeable in a liquid like carbon tetrachloride and suggested a possible quantitative relationship between the *intensity* of such wings and the *optical anisotropy* of the scattering molecules. Subsequent theoretical investigations by Manneback [2] have afforded quantitative expressions connecting the two phenomena in certain simple cases. Recent investigations by Raman and Bhagavantam [3] on the subject of light scattering in gases have further emphasised the importance of studying the *intensity* and polarisation characters of both Rayleigh and rotational Raman scattering as an aid to the verification and development of the theoretical aspects of the subject.

The above experiments and the theory are however confined to gaseous molecules and as such, leave the subject of liquid state untouched. It is proposed in this paper to extend the studies to liquids with a view to examine the applicability or otherwise of the above theories in such cases and eventually throw light on the nature of the liquid state. Two different aspects of the subject, *viz.*, (*i*) the aggregate intensity of the rotational wing in relation to the aggregate intensity of the Rayleigh scattering and (*ii*) the distribution of intensity in the wing itself will be dealt with here.

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[1] Nature, 122, 882, (1928).

[2] Z. f. Physik, 62, 224 (1930).

[3] Ind. J. Phys., 6, 358, (1931).

2. *Method of Measurement and Experimental details.*

The essential features of the method employed here have already been indicated by Raman and Bhagavantam.[4] The state of polarisation of the scattered light for any particular wave-length is spectroscopically determined by using very narrow and very wide slits successively. The difference between the two values constitutes a measure of the intensity of the rotational wing in relation to the pure Rayleigh scattering. The success of the method in practice, however, depends on the following conditions being fulfilled. In the case of the wide slit, the broad photographic image obtained on the plate should envelope the entire rotational wing to ensure the aggregate effect being observed. On the other hand, in the case of the narrow slit, the image should be so sharp that it constitutes only the Rayleigh scattering while the entire rotational wing is resolved from it and separated out. It is clear that the method breaks down when the rotation wing is spread out over a considerable region of the spectrum.

The following calculation, based on the assuption that all parts of the rotional wing exhibit a depolarisation of 6/7 when unpolarised incident light is used,[5] shows how the ratio of the aggregate intensity of the wing to that of the Rayleigh line may be deduced from the observed narrow and wide slit depolarisation values. As usual, Z represents the strong or the vertical component and X the weak or the horizontal component. We may represent the desired ratio by p and express it as

$$p = \frac{I_z\ (\text{Raman}) + I_x\ (\text{Raman})}{I_z\ (\text{Rayleigh}) + I_x\ (\text{Rayleigh})}$$

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[4] *Loc. cit.*

[5] Ind. J. Phys., 7, 79 (1932).

If ρ_n and ρ_w respectively represent the narrow and wide slit depolarisation values, we have

$$\rho_n=\frac{I_x\text{ (Rayleigh)}}{I_z\text{ (Rayleigh)}}\,;\quad \rho_w=\frac{I_x\text{ (Rayleigh)}+I_x\text{ (Raman)}}{I_z\text{ (Rayleigh)}+I_z\text{ (Raman)}}$$

Remembering that I_x/I_z (Raman) is 6/7, we can easily express p in terms of ρ_n and ρ_w in the following way:

$$p=\frac{13(\rho_w-\rho_n)}{(6-7\,\rho_w)\,(\rho_n+1)} \tag{1}$$

The experimental determination of ρ_w and ρ_n is made by interposing a nicol in the path of the scattered light before it enters the slit of a spectrograph. The spectra, one slightly above the other, are photographed on the same plate with the vibration axis of the nicol in the vertical and horizontal positions respectively. By trying different times of exposure for the one or the other, the intensities of the horizontal and the vertical components of the scattered light are rendered equal for any particular wave-length; actually, the measurements were made for the 4046 and 4358 A.U. of the mercury arc. The values for the two wave-lengths do not differ from one another. In this connection, it may be remarked that Krishnan and Sirkar[6] find such a constancy of depolarisation for different wave-lengths in benzene. Under such conditions, the depolarisation of the scattered light is given by the formula

$$(I_x/I_z)\times 100/D=\left(\frac{T_z}{T_x}\right)^{0\cdot 86}$$

In the above relation D represents the percentage depolarisation induced by the instrument itself, due to oblique refraction at the prism surfaces.

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[6] Ind. J. Phys., 6, 193 (1931).

In the above method, there are various difficulties and sources of error which may be briefly mentioned here. In the first place, it is easily seen from equation (1) that for liquids in which ρ_n approaches 6/7, ρ_w also approaches 6/7, and it becomes increasingly difficult to evaluate p accurately as it depends on a small and gradually vanishing quantity $(\rho_w-\rho_n)$. Another difficulty arises if there is a continuous background in the scattered light because, as the slit is opened, not only does the rotational wing fall on the top of the Rayleigh line, but also the aggregate intensity of the continuous spectrum present in the particular region. The stray light due to reflection from the sides of the containing vessel has to be carefully avoided by keeping the liquids in completely blackened containers of suitable shape and capacity and having clear windows only for illumination and observation. Another important source of error is that due to a lack of transversality of the illuminating rays and this is eliminated by using a small source of light in place of the usual 6-inch mercury arc. For a fuller discussion of the various sources of error and the experimental details, reference may be made to the recent papers of Raman and Bhagavantam already cited.

3. *Results.*

The liquids have been grouped into 3 divisions: (*i*) associating, (*ii*) non-associating, and (*iii*) viscous liquids. In the following table, the observed depolarisation values for the narrow and wide slits are given. The value of p which represents the ratio of the aggregate intensity of the rotational wing to that of the Rayleigh line is deduced with the help of equation (1) for each liquid and is given in the fifth column. The last column contains the value of p calculated from δ, the known optical anisotropy of the molecule in the liquid state, in a manner described in the following section.

TABLE I.

Liquids.	ρ_n	ρ_u	δ*	p experimental.	p theoretical.
(*a*) *Associating liquids*					
1. Formic acid	0·49	0·52	0·047	0·1109	0·3850
2. Acetic acid	0·385	0·40	0·036	0·0439	0·3028
(*b*) *Non-associating liquids*					
1. Benzene	0·34	0·425	0·022	0·2726	0·3510
2. Carbon disulphide	0·50	0·650	0·079	0·8964	0·4643
3. Carbon tetrachloride.	0·06	0·070	0·001	0·0223	0·0561
4. Acetone	0·18	0·25	0·009	0·1814	0·1940
5. Diethyl ether	0·055	0 08	0·003	0·0566	0·0725
6. Butyl alcohol	0·08	0·09	0·002	0·0224	0·0719
7. Iso butyl alcohol.	0·055	0·075	0·0017	0·0450	0·0602
8. Amyl alcohol	0·065	0·080	0·0023	0·0337	0·0640
9. Propyl acetate	0·160	0·20	0·0064	0·1508	0·1695
(*c*) *Viscous liquids*					
1. Salol	0·75	0·75	high	0	...
2. Glycerine	0·16	0·29	...	0·3660	...

* The values are taken from I. R. Rao, Ind. Jour. Phys., 2, 61, 1927.

4. *Discussion of the Results.*

Both classical[7] and quantum[8] theories of the Raman effect give the following expressions for the intensities of various branches of scattering.

$$I_z(\text{Raman}) = E^2\gamma^2 . \frac{1}{15}; \quad I_z(\text{Rayleigh}) = E^2\left(\mu^2 + \frac{1}{45}\gamma^2\right)$$

$$I_y = I_x(\text{Raman}) = E^2\gamma^2 . \frac{1}{20}; \quad I_y = I_x(\text{Rayleigh}) = E^2\gamma^2 . \frac{1}{60}$$

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[7] Ind. J. Phys., 6, 331 (1931).

[8] Z. f. Physik, *loc. cit.*

The expressions are valid for diatomic gaseous molecules when incident plane polarised light is used and may easily be modified for the case of incident unpolarised light with the following results :

Aggregate intensity of the rotational wing $= 13/60 E^2 \gamma^2$

Aggregate intensity of the Rayleigh scattering $= E^2 \mu^2 + \frac{13}{180} E^2 \gamma^2$

By substituting (A—B) for γ and $\left(\frac{A+2B}{3}\right)$ for μ in the above expressions and neglecting the second term of the Rayleigh scattering,[9] we may rewrite the value of p which represents the ratio of these two quantities as

$$p = \frac{39}{20} \cdot \frac{(A-B)^2}{(A+2B)^2} \backsim 2\delta.$$

Recent investigations by Bhagavantam on gases however indicate that there is actually present only about half the expected rotation wing and as such the above relation between p and δ may be written as $p \backsim \delta$. In liquids, however, the relation between p and δ is not so simple and a modified calculation has to be made taking into account the compressibility of the liquid. After transferring half the intensity of the rotation wing to the Rayleigh scattering as in the case of gases we may write the value of p as

$$p = \frac{13/120\gamma^2}{\mu^2 + 65/360\gamma^2}$$

This is easily evaluated in terms of δ with the help of the relation

$$\rho_w = \frac{I_x \text{ (Rayleigh + Raman)}}{I_z \text{ (Rayleigh + Raman)}} = \frac{2/15\gamma^2}{\mu^2 + 7/45\gamma^2} = \frac{6\delta}{\frac{5RT\beta n}{N} + 7\delta}$$

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[9] This is justified because γ is usually small in comparison with μ.

and written as

$$p = \frac{39\delta}{\frac{40RT\beta n}{N} + 65\delta} \qquad \ldots \quad (2)$$

the correctness of which is easily seen by the fact that if $\frac{RT\beta n}{N}$ is replaced by unity and the second term of the denominator neglected, the relation reduces to $p \sim \delta$ which we have already noted in the case of gases. The p values calculated from the relation (2) taking the known compressibility and δ for each liquid are given in the last column of Table I. A comparison of the figures in the last two columns shows that the expected intensity of the rotation wing is observed in a number of liquids, notable examples being benzene and acetone. In other non-associating liquids, the observed intensity of the rotation wing is usually somewhat smaller than the calculated value thus indicating a certain impedance to free rotation in the liquid state.

The associating and the viscous liquids stand however on a different footing as the observed value of p in these cases is nearly zero, contrary to the theoretical expectations. This indicates a *negligible* rotation wing, and suggests the presence of a large impedance to molecular rotation in these classes of liquids. The large change in the depolarisation exhibited by glycerine is attributable to an appreciable amount of continuous background in the scattered spectrum and hence the result cannot be interpreted as indicating the presence of free rotation.

5. *Intensity Distribution in the Rotation Wing.*

It is well-known that for gases with low moment of inertia such as hydrogen, oxygen, nitrogen, etc., it is possible even with an ordinary spectrograph, to obtain discrete rotation lines working at sufficiently low pressures. Contrary to this, however, liquid hydrogen is, so far, the only liquid for which discrete rotation lines have been observed.[10] Recently, Meyer and Ramm,[11] working with a resolving power more than sufficient to resolve the rotation lines of benzene—if the moment of inertia of the rotator was really due to a single molecule—did not succeed in separating them from each other. The failure may be due either (*i*) to a possible circumstance that the scattering units in liquids possess a much higher moment of inertia than single gaseous molecules, thus rendering the resolving power employed insufficient or (*ii*) to an inherent absence of discrete quantisation of rotational energy in liquids owing to the density of packing. These questions are peculiar to the liquid state and are intimately connected with the manner in which the intensity is distributed in the rotation wing. The present section will be devoted to an experimental investigation of the intensity distribution in the wing itself.

Benzene is selected for the purpose and a grating of one metre focal length is used to obtain the scattered spectrum. The resolving power was such that lines about one wave-number apart could be easily separated. The liquid is contained in a long Wood's tube of 18 inches length with an inner diameter of 1 inch closed by a plane glass window at one end and a drawn-out horn at the back to provide a suitable background. The tube is painted black, leaving an opening along its length to allow the light from an 18-inch mercury arc placed close to it. A chief difficulty is the broadening of the true Rayleigh line on long expoures thus preventing any reliable conclusions being drawn with regard to the intensity distribution in its immediate vicinity. This is overcome by minimising the time of exposure as far as possible,[12] and eliminating very completely the reflected light with the above precautions. In the actual experiment λ4046 is made use of and is found to possess a breadth of about 3 or 4 wave numbers after the necessary exposure. The choice of this line in preference to the more intense λ4358 is guided by the fact that it is a single line unlike the latter which is accompanied by two other companions.

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[10] McLennan, Smith and Wilhelm, Trans. Roy. Soc., Canada, 23, 247 (1929).

[11] Phys. Zeit., 33, 270 (1932).

[12] An exposure of about 1 or 2 hours is found to be sufficient to bring out the wing in practice.

The essential results may be stated as follows :

The intensity distribution curve does not show any discontinuity: there is a falling off in intensity of the rotation wing starting from a maximum at the Rayleigh line. The intensity appears to become quite inappreciable after about 50 or 60 wave-numbers.[13]

These features seem to be characteristic only of the liquid state as contrasted with the gas where both theory and experiment indicate the presence of two distinct intensity maxima, one on either side of the Rayleigh line and well separated from it. The distribution of intensity in the case of a gas is controlled by the distribution of molecules in various rotational states according to equation (3) and the maximum occurs

$$N_k = (2K+1)e^{-\sigma K(K+1)} \tag{3}$$

approximately at a place where the value of K is such that the number of molecules in that state is a maximum. The value of K fulfilling the above conditions may easily be found after differentiating the foregoing equation and written as

$$K^* = \frac{1}{\sqrt{h^2/4\pi^2 I_0 KT}} - \frac{1}{2}$$

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[13] The last result is also borne out by the depolarisation measurements with varying slit widths as it is found by the author that there is no further increase in the depolarisation after the image has broadened to the extent of about 50 wave-numbers on either side.

The distance of the corresponding rotation line from the Rayleigh line may be expressed as 6B+4BK, where B stands for $h/8\pi^2 c I_0$. Substituting and simplifying, we get the following expression for the wave-number difference ν of the maximum from the Rayleigh line :

$$\nu^* = {}^{h}/{}_{2\pi^2 c I_0} + \left(1 \, /_{\pi c}\right) \sqrt{{}^{KT}/\, I_0} \qquad (4)$$

It is interesting to note that this expression differs from the value deduced on the basis of the classical statistics only by a small term, *i.e.*, $h/2\pi^2 c I_0$. When this is evaluated for benzene taking its moment of inertia[14] to be 156×10^{-40} the value of ν comes out as 18·0 cms,$^{-1}$ a result which is in complete disagreement with the experiment. Such a disagreement between the theory and experiment suggests that either (*i*) the statistics obeyed by the gas molecules is totally inapplicable to the liquid state or (*ii*) that the scattering centres are not single molecules but clusters of them having a large moment of inertia. In the latter case, the intensity maximum would be so close to the Rayleigh line that difficulties such as its spreading to 4 or 5 wave-numbers prevent the discontinuity being detected. A tentative calculation on the basis of equation (4) shows that the moment of inertia required to shift the intensity maximum to within 4 or 5 wave-numbers of the Rayleigh line is about ten times that of a single molecule.

The actual state of affairs in a liquid may even be more complicated in that, molecular groups of still higher or lower moment of inertia may also be present, the actual rotation pattern obtained being a superposition of all the effects.

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[14] Different values of I_0 have been attributed to benzene by different authors. Thus Meyer and Ramm gave it as 270×10^{-40}. The present value (*i.e.*) 156×10^{-40} is based on the assumption that the benzene ring has a plane structure having the dimensions given by Mrs. Lonsdale (Proc. Roy. Soc., 123, 494, 1929.)

These points and other allied topics are under investigation and will form the subject matter of a further communication.

In conclusion, the author wishes to express his best thanks to Prof. Sir C. V. Raman, Kt., F. R. S., N. L., for his keen interest and guidance during the progress of the work.

28

Experimental Study of the Duration of Contact of an Elastic Hammer striking a Damped Pianoforte String.*

By

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(Plates XXV, XXVI and XXVII.)

ABSTRACT.

In this paper the variation of the duration of contact for one hard, two elastic and a felt hammer, each being of the same weight, has been studied, photographically, for different striking distances of a string of length 600 cms. The time record on the photograph has been made by a fork of frequency 200. It is found that in all cases the duration of contact varies discontinuously as the striking distance increases. In studying the effect of elasticity (E) of the hammer on the duration of contact, when striking at the mid-point, it is found that, at first the duration of contact increases, then attaining a maximum value, slowly decreases and tends to be constant as (E) is further increased. As regards the effect of the radius of curvature (r) of the surface of contact of the hard hammer striking at mid-point it is found that the duration of contact for lower values of (r) is constant, and then increases as (r) increases and finally becomes constant for large values of (r). The damping of the string is found to have little effect, on the duration of contact as also follows from the author's theory. In the case of the felt hammer it is found that the duration of contact multiplied by the fifth root of the velocity of impact, to be constant, as required by Hertz's theory of impact.

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* Indian Science Congress, 1932.

The theoretical side of the problem of the pianoforte string is more or less completely studied by Kar and the writer[1] and the writer[2] alone, in a series of papers, where it has been shown that the other theories known, are the special cases of the above. In a number of experimental papers by the writer,[3] the duration of contact in the case of the hard, massive, hammers, and the energy lost by an elastic hammer has been studied. The present paper gives an account of the systematic study of the duration of contact, in the case of hard, elastic and felt hammers.

Before describing the present experiment it will be useful to give a brief account of the experimental work already done on the acoustics of the pianoforte. In doing so, it will be convenient to divide the subject, into the following: (1) Determination of the duration of contact between the hammer and the string, (2) Displacement of the struck point, during impact, (3) Analysis of the note emitted, (4) The energy lost by the hammer during impact, (5) The nature of the vibration set up in the sound board and the bridge.

(1) In the year 1886 C. K. Weak,[4] measured the duration of contact, between a felt hammer and a pianoforte string, with the help of a ballistic galvanometer, and found that the duration of contact decreases as velocity of impact increases. Then in the year 1894, W. Kaufmann[5] using the photographic method, measured the duration of contact in the case of a hard hammer, striking at the end, and at the mid-point of a string and compared with his theoretical values. In the case of the felt hammer, he also got the same thing as Weak. In the year 1920 Raman and Banerjee[6] using the same electrical method of Weak, measured the duration of contact in the case of the hard hammer and pointed out for the first time that the duration of contact goes on discontinuously fluctuating, as the striking distance goes on increasing from one end. Later on R. N. Ghosh[7] and his co-workers measured the duration of contact in the case of a

felt hammer, striking at an end, and have shown that it changes continuously, as the striking distance increases from one end. Then comes George,[8] who has made a systematic study of the duration of contact in the case of a hard hammer by Duddal oscillograph and arrived at the same conclusion as Raman. The beautiful photograph of the variation of the current in the oscillograph is a proof of the pressure fluctuation of the hammer during contact. He has further shown that for the hard hammer striking at a given distance of the string, the duration of contact remains constant over a wide range of hammer velocity. Banerjee and Ganguli[9] photographically determined the duration of contact for a hard hammer striking near an end, and attempted to show the superiority of Das's theory—a particular case of ours—over Kaufmann's end theory. They have further shown that the shorter segment of the string vibrates during impact. This however was first shown by Kaufmann long before them, photographically, though he could not give any satisfactory explanation of it (*cf*. photograph. (31*a*) (31*b*) of his paper,[5] pts. 7). This however can easily be explained from our theory[2] (l.c.). The writer[3] has shown the prominent nature of the discontinuous fluctuation of the duration of contact with two massive hammers. Further it has been shown that duration of contact changes discontinuously from epoch to epoch with change of mass-ratio of the hammer.

(2) The measurement of the displacement of the struck point during contact, at different instants in the case of a hard hammer was done by George[10] long after Kaufmann.[5] Kaufman has compared his experimental results with his theory, when hammer strikes only at the middle, for two different velocities of impact. George compared his results for mid-point, and for the struck point very near an end, with different theories then existing and found better agreement with Kaufmann.

(3) Hipkin[11] first observed that *n*th harmonic is not absent when the string is struck at (l/n), for a felt hammer. Berry[12] first made a systematic study of the amplitude of the fundamental for different struck points and has found that it is maximum when struck at about $(2l/9)$. He has also shown that for this particular struck point the amplitude of the fundamental of the sound board is minimum. Later on R. N. Ghosh[13] has shown that the amplitude of the fundamental is maximum, at the point, where duration of contact has half the value of the time period of the gravest note of the string. In 1925 George[14] has made a closer study of the same thing, and has shown that, the position of the striking point for which the fundamental is maximum, is nearer the bridge, the greater the relative mass of the hammer. Before George, Dutta,[15] directly measured the amplitude of the different harmonics, with a microscope, after stopping the lower harmonics by touching at suitable points and has shown that his experiment is in close agreement with Das's theory. Later on Kar[16] and his co-workers have repeated the experiment of Dutta in the same manner, and have pointed out that such a close agreement with theory as shown by Dutta is not possible with such a rough method of damping the harmonics and measuring the amplitudes.

(4) The loss of energy by a hard hammer during impact for different striking distances was studied by George and Beckett[17] for different mass ratios of the hammer. The present writer[8] has also studied the same thing for different elastic hammers and for constant mass ratios and has got a number of very interesting curves.

(5) Berry[18] has made first an attempt to study the vibration of the sound-board and has shown that two portions of the sound board divided by the free bridge vibrate in the same phase. He also remarks that the string and the sound board form a coupled system during vibration. Next R. N. Ghosh has repeated the same experiment and has arrived at

the same conclusion. Recently L. D. Mahajan[19] has made a detailed study of the vibration of the sound board and the effect of the soft pedal.

In future the author hopes to make a detailed study of the other cases discussed above.

Now, we shall proceed to give the details of the photographic study of the duration of contact, recently made by the writer, in the case of hard, elastic and felt hammers. The following are the items which have been systematically studied :—

(*a*) The variation of the duration of contact with variation of the striking distance from one of the ends of the string, in the case of hard, elastic and felt hammers.

(*b*) The variation of the ratio in which the vibration curve at the struck point just after impact, is divided by the maximum peak with the distance from the nearer end.

(*c*) The variation of the duration of contact with the elasticity of the hammer when struck at the mid-point of the string.

(*d*) The variation of the duration of contact with the variation of the radius of curvature of the surface of contact, for the mid-point.

(*e*) The effect of damping on the duration of contact, in the case of a hard and pointed hammer striking at the mid-point.

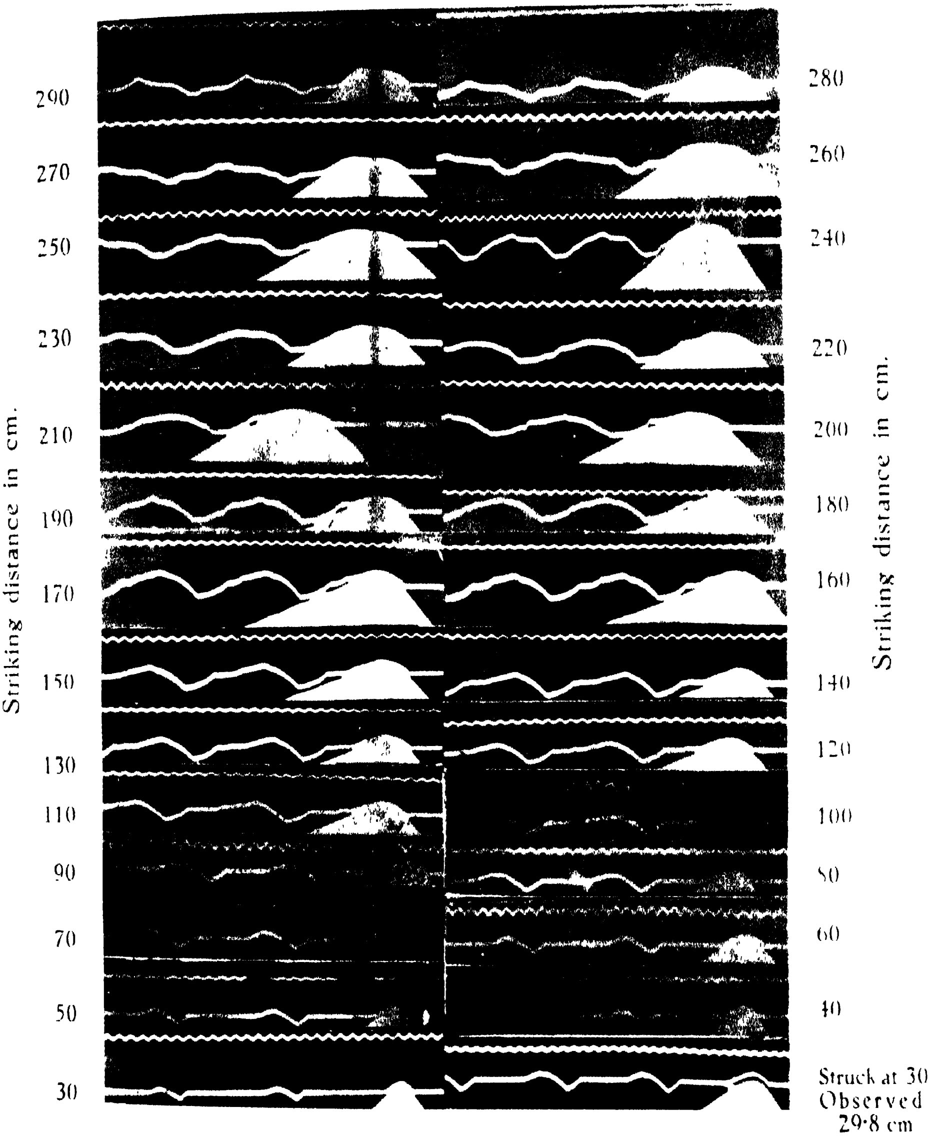
(*f*) The effect of the velocity of impact of the felt hammer, on the duration of contact for the mid-point.

The experimental arrangement is more or less the same as described in the previous paper [8]. The only necessary change made is the sliding camera to photograph the motion of the hammer and the string simultaneously. The velocity of the photo-carrier which moves under the difference of weights at the two sides, is maintained constant, by allowing the weights to travel through a viscous liquid and at the same time leaving the requisite weight at rest during movement as in Atwood's machine. The time is measured from the shadow photographic waves of the fine aluminium pointer attached to one of the prongs of an electrically maintained fork of frequency 200. Light from an arc facing the narrow slit of the camera vertically downwards, is obstructed by the pointer and the point of contact of the hammer and the string, which cast their shadow on the photo paper inside. The outlines of the white patches in the photograph describe the motion of the hammer. The string before impact remains at rest, which is shown by the straight portion of the vibration curve towards the right of the hammer's shadow in the photograph, and set in regular vibration just after hammer leaves the string. The small regular waves overhead each photograph are the waves due to vibrating fork.

In all these cases, except in the case (F) the velocity of impact has been kept constant, by allowing the hammer to impinge on the string from a constant distance. A pendulum arrangement has been made for the hammer, detailed description of which is given in one of our published papers.[3] The arc along which the hammer moves is measured from the magnified shadow of the hammer over a graduated translucent scale. Ample precautions are taken before each photograph, so that the cylindrical surface of contact of the hammer, strikes the string just perpendicularly and that, there is no overlapping of shadows of the hammer and the string, just before and after the contact, otherwise, this will introduce serious error in the measurement.

In order to obtain the simultaneous photograph of the motion of the hammer and the string, a great deal of care has been taken in releasing in time the photo-carrier and the hammer from their respective mechanical catches. The measurement of the duration of contact has been made by a travelling microscope reading up to ·001 cms., the number of waves traced just over head, by the fork, within the same

Elastic hammer (E=49 21)



Struck at 30
Observed
29·8 cm

length of the hammer's shadow in contact with that of the string, gives the duration of contact.

The details of the construction of the elastic hammer are given in a previous paper.[8] The springs of different diameters, that have been fitted in the hammer are made of steel wire of 20 S.W.G., each of 20 turns. The weight in gm. to produce unit compression of this hammer has been measured by a microscope from the compression produced by a known weight. This weight in gm., multiplied by the gravitational constant (978), gives the elastic constant of the hammer. Results :—

Length of the string (l)	600 cms.
Line density (ϱ)	·0495 gm./cm.
Mass of the hammer (m)	21·21 gms.
${}^{l\varrho}/_{m} = {}^{m'}/_{m}$	1·4
Tension of the string	38488·7 gms. wt.

(A) The hammers are released from a fixed distance and made to strike against the string from one end to the mid-point, at a regular interval of 10 cms. The duration of contact for different struck points and for different hammers are given in table I and the photographs (see Pls. XXV and XXVI) are also given. It has been found, for the striking distances between 140 cms. to 240 cms. and at 130 cms. and 140 cms. in the case of the hard hammer, between 140 to 240 cms. in the case of the elastic hammer of $E=277·7\times 978$, at 70 cms. and 100 to 230 cms. for the elastic hammer of $E=49·21\times 978$, and finally at 150, 190, and at 200 cms. in the case of the felt hammer, that there are double or triple contacts before the hammers finally leave the string. It is obvious from the pressure equations[2] that these phenomena are due to the influence of the reflected waves from the remoter end that overtakes the hammers.

Now, it has already been found that the pressure due to the hammer is a function of time, $f(t)$ and the duration of contact is a root of the equation $P=f(t)=0$. But the expression for the pressure at an epoch higher than the second, involves higher powers of t. So this equation $f(t)=0$ gives multiple root of which more than one may be real and positive. In that case it is more logical to define the real duration of contact as the greatest positive root of the equation $f(t)=0$. After this maximum value of the root the pressure becomes negative.

The experimental values of the different duration of contacts, measured each from the beginning of the first contact and also the durations of the different separations are given in the same table I. The curve showing the variation of the real duration of contact as defined above, with the striking distance is shown in fig. (1). In all these cases the

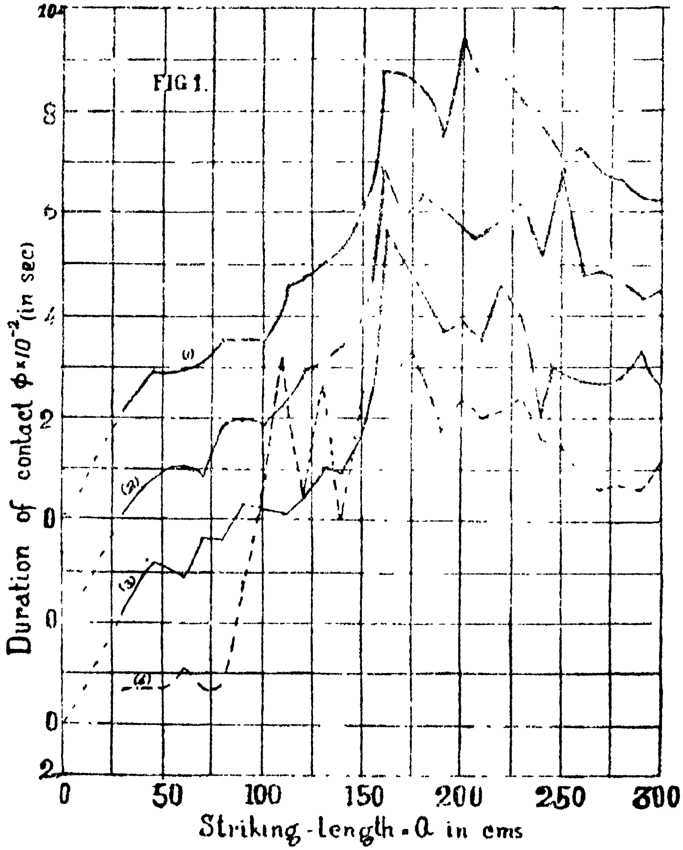


FIG. 1.

PLATE XXVI

Felt hammer.

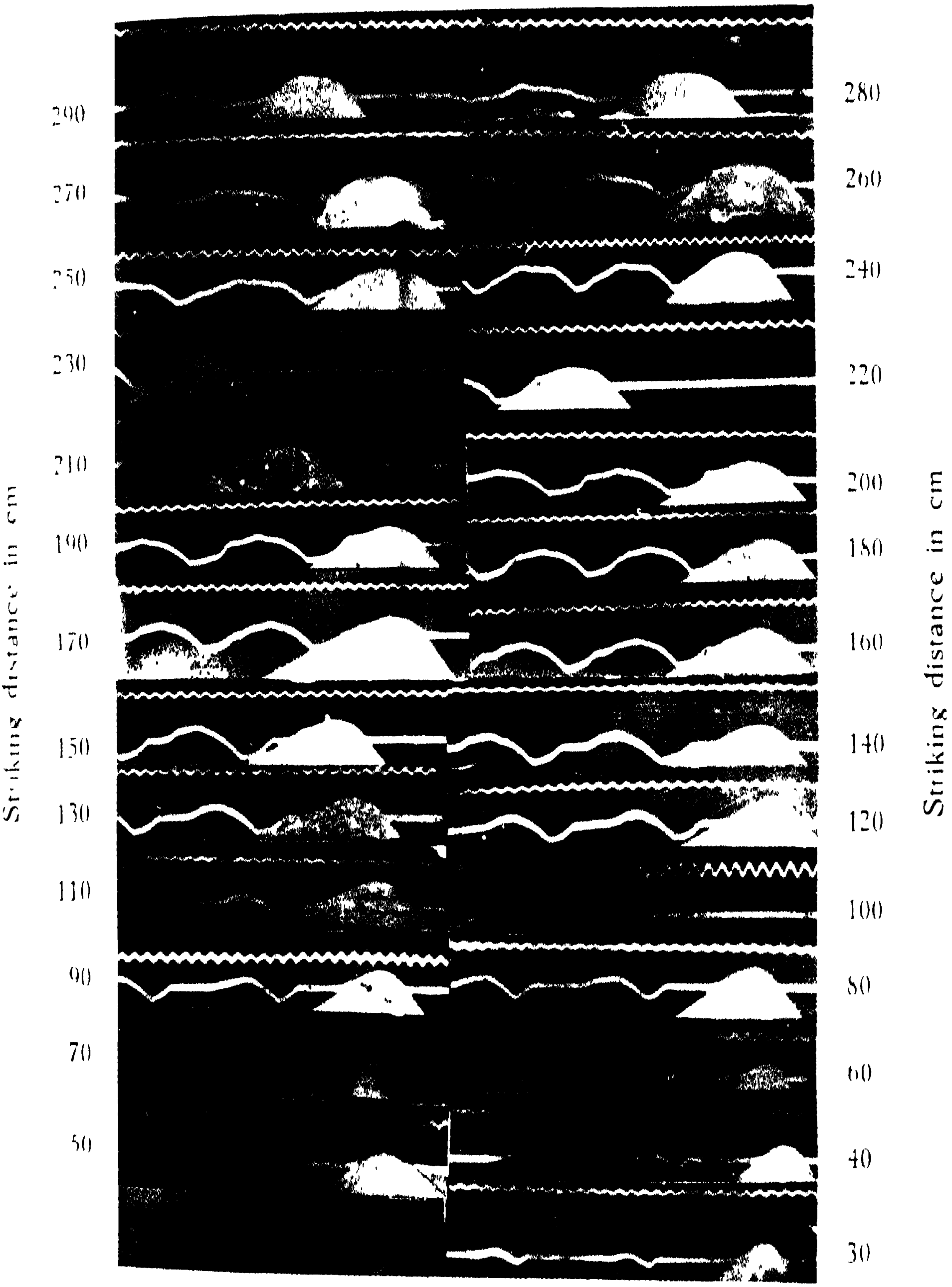


TABLE I.

Velocity before impact 45·5 cm/sec.
Radius of curvature of the surface of contact 1·585 cms.
Damping coefficient of the string ·186.

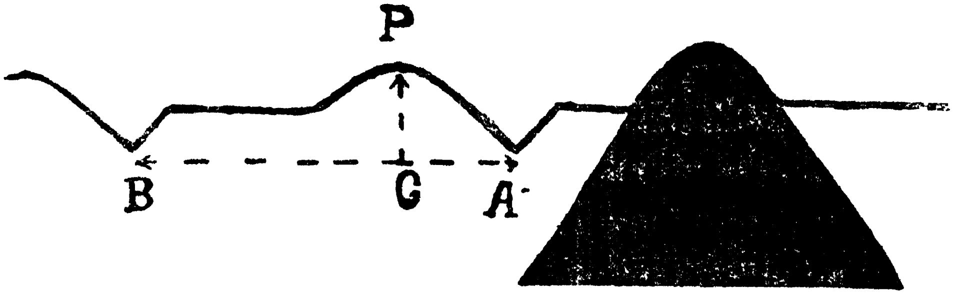
Striking distance 'a' in cms.	Hard (1)		Elastic.				Felt (4)	
			(2) E=277·7 × 978		(3) E=49·21 × 978			
	Duration of contact in sec. $\times 10^3$	Duration of Separation in sec. $\times 10^2$	Duration of contact in sec. $\times 10^3$	Duration of Separation in sec. $\times 10^3$	Duration of contact in sec. $\times 10^2$	Duration of Separation in sec. $\times 10^2$	Duration of contact in sec. $\times 10^3$	Duration of Separation in sec. $\times 10^2$
30	1·1035	...	1·0535	...	1·0995	...	1·8580	...
40	1·3620	...	1·3260	...	1·4760	...	1·8550	...
50	1·4335	...	1·4935	...	1·5570	...	1·8560	...
60	1·4835	...	1·5295	...	1·4610	...	2·0325	...
70	1·5885	...	1·4225	...	(1) 1·4645	...		
					(2) 1·8190	·237	1·8025	...
80	1·7655	...	1·9360	...	1·8060	...	1·9170	...
90	1·8255	...	1·9610	...	2·1765	..	2·9170	...
100	1·7345	...	1·9615	...	2·1415	...	3·6525	...
110	2·1030	...	2·1205	...	2·0855	...	5·1445	...
120	2·3575	...	2·4050	...	2·1985	...	3·7765	...
130	2·5290	...	2·5615	...	2·5355	...	(1) 3·5540 (2) 4·8125	·721
140	(1) 2·0665 (2) 2·6620	·061	(1) 2·1580 (2) 2·7275	·166	2·4755	...	3·500	...
150	(1) 2·3365 (2) 3·2700	·064	(1) 2·2750 (2) 3·0420	·194	2·8850	...	(1) 3·4755 (2) 4·7550	·565
160	(1) 2·2590 (2) 3·0290 (3) 4·4255	·367 ·882	(1) 2·3680 (2) 3·0808 (3) 4·4550	·312 ·832	(1) 2·0435 (2) 3·0855 (3) 4·4725	·405 ·875	4·8560	...

TABLE I (Continued).

Striking distance 'a' in cms.	Hard. (1)		Elastic.				Felt. (4)	
			(2) E=277·7 × 978		(3) E=49·21 × 978			
	Duration of contact in sec. $\times 10^2$	Duration of Separation in sec. $\times 10^2$	Duration of contact in sec. $\times 10^2$	Durationon Separation in sec. $\times 10^2$	Duration of contact in sec. $\times 10^2$	Duration of Separation in sec. $\times 10^2$	Duration of contact in sec. $\times 10^2$	Duration of Separation in sec. $\times 10^2$
170	(1) 2·2350 (2) 4·3955	1·492	(1) 2·2525 (2) 3·9710	1·443	(1) 2·6800 (2) 4·5795	1·384	5·045	...
180	(1) 2·5440 (2) 4·2125	1·011	(1) 2·5520 (2) 4·1900	·935	(1) 2·6550 (2) 4 2690	·865	4·9425	...
190	(1) 2·5675 (2) 3·7760	·776	(1) 2·4680 (2) 4·0565	·909	(1) 2·5395 (2) 3·8720	·792	(1) 1·8320 (2) 4·386	·563
200	(1) 2·3830 (2) 4·7275	·944	(1) 2·5520 (2) 3·8530	·738	(1) 2·7625 (2) 3·7700	·586	4·6420	...
210	4·2410	...	(1) 2·4685 (2) 3·8015	·881	(1) 2·5570 (2) 3·7740	·649	4·500	...
220	4·3385	...	(1) 2·8050 (2) 3·9135	·387	4·300	...	(1) 2·9100 (2) 4·5900	·267
230	(1) 2·8320 (2) 3·6460 (3) 4·1350	·454 ·091	(1) 2·8475 (2) 4·1225	·507	(1) 2·7350 (2) 3·9970	·375	4·7185	...
240	(1) 3·0160 (2) 3·8665	·229	(1) 2·7620 (2) 3·5965	·270	3·0040	...	4·3400	...
250	3·5650	...	3·4800	...	3·4600	...	4·2600	...
260	3·6150	...	3·4950	...	3·3750	...	3·9400	...
270	3·4000	...	3·4500	...	3·3550	...	3 8450	...
280	3·2300	...	3·3500	...	3·4150	...	3·8350	...
290	3·1050	...	3 2200	...	3·6850	...	3·8200	...
300	3·1300	...	3·2885	...	3·3050	...	4·0595	...

curve is discontinuously fluctuating and tends to approach zero as the struck point approaches the end, but in the case of the felt hammer, it attains constant value at the end which is evidently due to the deformation of its surface of contact. Further the multiple contact in the case of the felt hammer during impact is a striking proof of the discontinuous fluctuation of the pressure even for a soft hammer, which is however contrary to the assumption made by the previous workers.

(B) The ratio AC/AB (fig. below) is measured with a microscope. The variation of this ratio with the striking distance is given in table II, and the corresponding curves



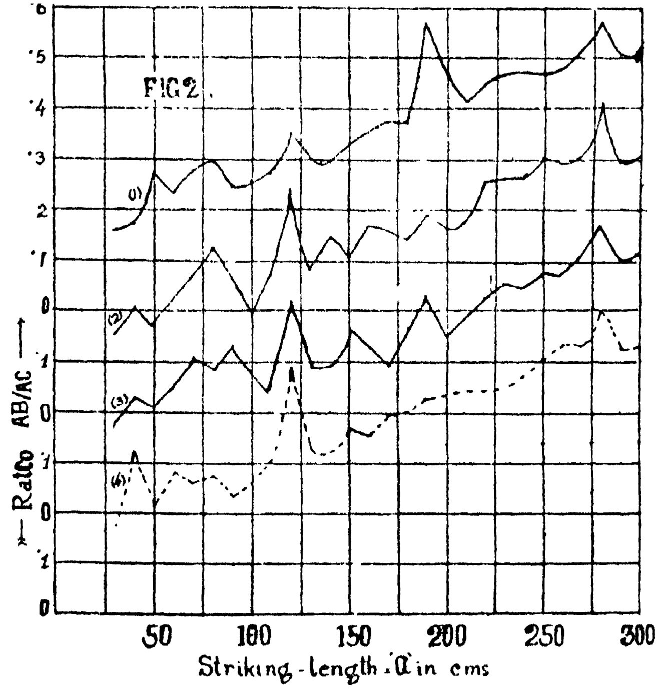


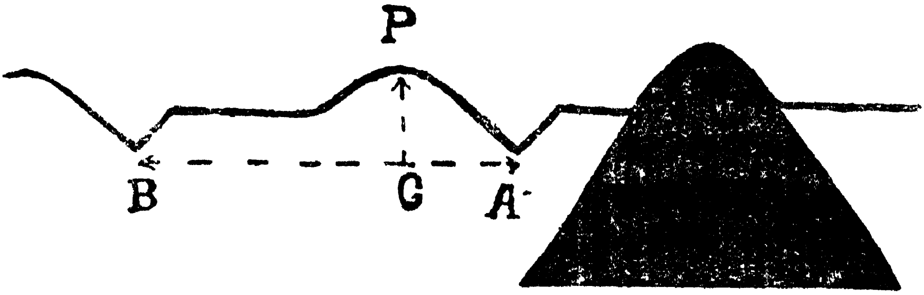
FIG. 2.

TABLE I (Continued).

Striking distance 'a' in cms.	Hard. (1)		Elastic.				Felt. (4)	
			(2) E = 277·7 × 978		(3) E = 49·21 × 978			
	Duration of contact in sec. × 10²	Duration of Separation in sec. × 10²	Duration of contact in sec. × 10²	Durationon Separation in sec. × 10²	Duration of contact in sec. × 10²	Duration of Separation in sec. × 10²	Duration of contact in sec. × 10²	Duration of Separation in sec. × 10²
170	(1) 2·2350 (2) 4·3955	1·492	(1) 2·2525 (2) 3·9710	1·443	(1) 2·6800 (2) 4·5795	1·384	5·045	...
180	(1) 2·5440 (2) 4·2125	1·011	(1) 2·5520 (2) 4·1900	·935	(1) 2·6550 (2) 4·2690	·865	4·9425	...
190	(1) 2·5675 (2) 3·7760	·776	(1) 2·4680 (2) 4·0565	·909	(1) 2·5395 (2) 3·8720	·792	(1) 1·8320 (2) 4·386	·563
200	(1) 2·3830 (2) 4·7275	·944	(1) 2·5520 (2) 3·8530	·738	(1) 2·7625 (2) 3·7700	·586	4·6420	...
210	4·2410	...	(1) 2·4685 (2) 3·8015	·881	(1) 2·5570 (2) 3·7740	·649	4·500	...
220	4·3385	...	(1) 2·8050 (2) 3·9135	·387	4·300	...	(1) 2·9400 (2) 4·5900	·267
230	(1) 2·8320 (2) 3·6460 (3) 4·1350	·454 ·091	(1) 2·8475 (2) 4·1225	·507	(1) 2·7350 (2) 3·9970	·375	4·7185	...
240	(1) 3·0160 (2) 3·8665	·229	(1) 2·7620 (2) 3·5965	·270	3·0040	...	4·3400	...
250	3·5650	...	3·4800	...	3·4600	...	4·2600	...
260	3·6150	...	3·4950	...	3·3750	...	3·9400	...
270	3·4000	...	3·4500	...	3·3550	...	3 8450	...
280	3·2300	...	3·3500	...	3·4150	...	3·8350	...
290	3·1050	...	3 2200	...	3·6850	...	3·8200	...
300	3·1800	...	3·2885	...	3·3050	...	4·0595	...

curve is discontinuously fluctuating and tends to approach zero as the struck point approaches the end, but in the case of the felt hammer, it attains constant value at the end which is evidently due to the deformation of its surface of contact. Further the multiple contact in the case of the felt hammer during impact is a striking proof of the discontinuous fluctuation of the pressure even for a soft hammer, which is however contrary to the assumption made by the previous workers.

(B) The ratio AC/AB (fig. below) is measured with



a microscope. The variation of this ratio with the striking distance is given in table II, and the corresponding curves

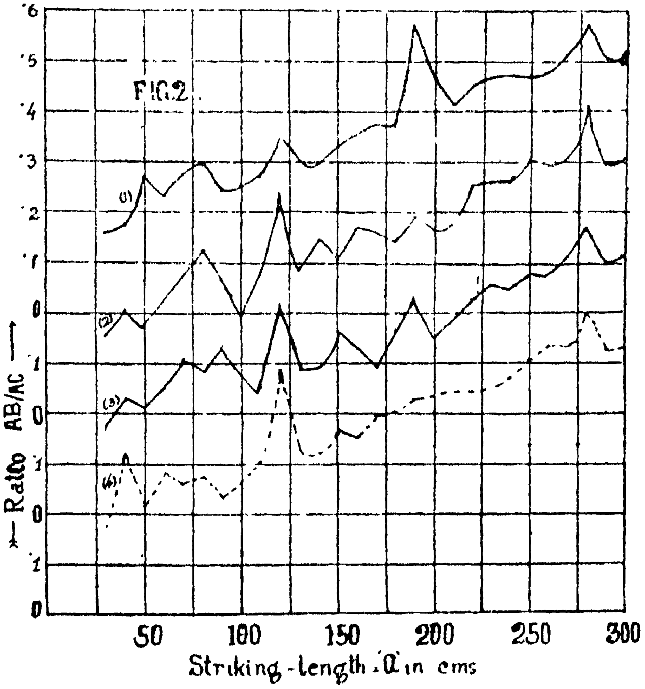


FIG. 2.

are shown in fig. (2). It is found from the curve that the position of the maximum peak in the wave form, also fluctuates discontinuously with the striking distance. A more detailed study of the phenomenon especially for the different mass-ratio and elastic constants of the hammer will be made by the author in near future.

TABLE II.

Striking Distance. 'a'	Ratio (AC/AB), 10^3				Striking Distance. 'a'	Ratio (AC/AB). 10^3			
	(1)	(2)	(3)	(4)		(1)	(2)	(3)	(4)
30	163	158	178	176	170	379	362	296	395
40	173	209	229	323	180	371	341	366	400
50	277	176	209	216	190	569	393	423	421
60	236	226	257	282	200	...	363	375	429
70	279	267	308	260	210	414	376	381	...
80	297	325	282	277	220	451	457	421	...
90	243	236	335	232	230	466	460	451	...
100	257	190	280	...	240	486	460	449	474
110	267	275	251	305	250	473	502	472	502
120	353	440	421	393	260	...	483	477	538
130	301	290	283	327	270	511	505	510	533
140	299	343	290	320	280	574	611	568	599
150	329	309	364	364	290	500	405	500	521
160	352	372	328	349	300	500	501	510	531

(C) The effect of the elasticity of the hammers on the duration of contact has been studied in the same way as before. The springs of different diameters are made from a steel wire of 20 S.W.G. They are fitted one after another in the hammer and the corresponding elastic constants are determined in the manner stated before. The mass of the hammer has been kept constant throughout this experiment, so also the velocity of impact and the surface of contact of the hammer. The results for mid-point only, are given in table III and the

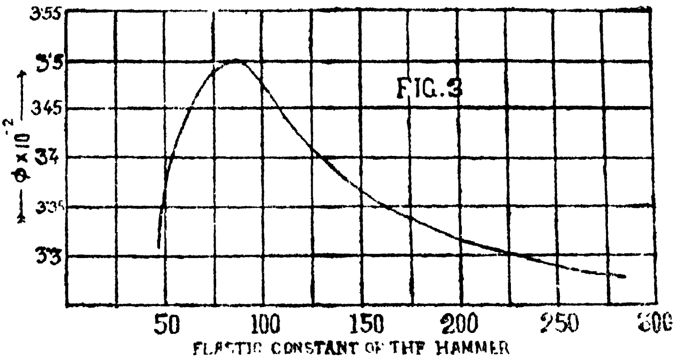


FIG. 3.

curve showing the variation of (ϕ) with (E) is given in fig. (3). It is found that as (E) increases, ϕ increases, attains a maximum value, and finally decreases and tends to be constant for higher values of (E), *i.e.*, when the hammer is hard. This fact may easily be interpreted by solving graphically Eq. (35) for different values of E. (Phil. Mag. Vol., 12, p. 683, 1931).

TABLE III.

Diameter in cm of spring.	Wt. in gm. of spring.	E/978	$\phi \times 10^2$
1·42	2·85	49·31	3·305
1·36	2·65	55·14	3·400
1·18	2·41	79·36	3·495
1·15	2·22	87·71	3·501
1·03	2·08	125·0	3·408
·99	1·97	162·0	3·351
·97	1·85	204·04	3·313
·84	1·55	277·7	3·288
...	...	∞	3·133

(D) In order to study the effect of the radius of curvature (r) of the hammer-head on the duration of contact at mid-point in the case of a hard hammer, semicylindrical shells of different curvatures have been prepared by pressing out a thick aluminium sheet. The height of the cylindrical surfaces are made very small (about three times the diameter of the string), in order to minimise the over-lapping of shadow of the hammer and the string as stated before. These have been used, one after another as the hammer-head and the corresponding durations of contacts have been determined. The results showing the variation of ϕ with (r) are shown in table IV, the corresponding curve is given in fig. (4) and the photographs are given in Pl. XXVII. It is found that for smaller values of (r), ϕ remains constant, then slowly increases with (r) and finally becomes constant for much higher values.

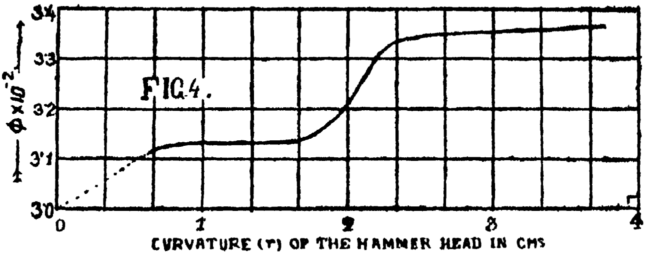


FIG. 4.

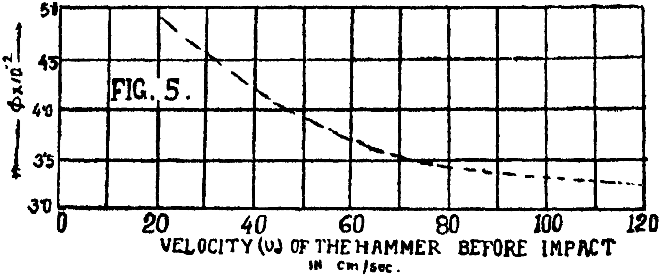
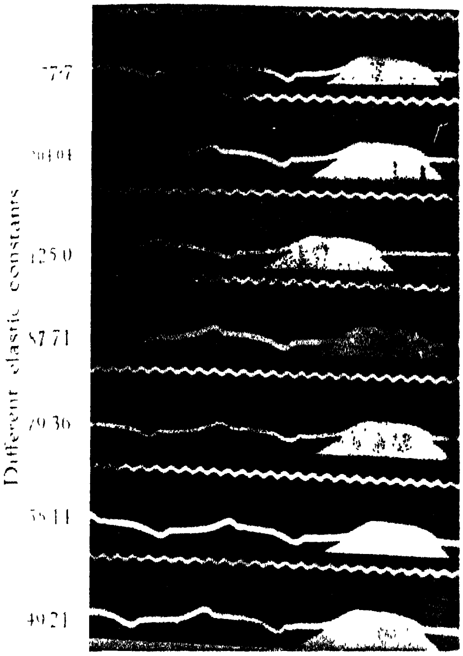


FIG. 5.

(E) In order to study the effect of damping on the duration of contact in the case of the wedge shaped hard hammer, striking at the mid-point of the string, we have first made the string to vibrate and the corresponding vibration curve is photographed, by allowing the photo-carrier to move slowly as to record the largest number of vibrations. The coefficient

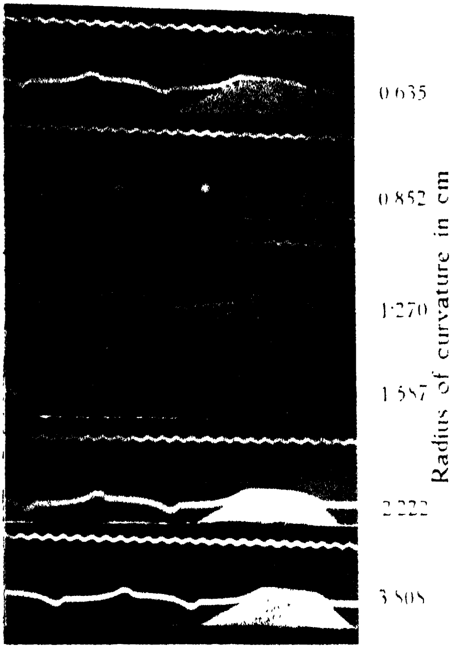
(a)

Elastic hammer.

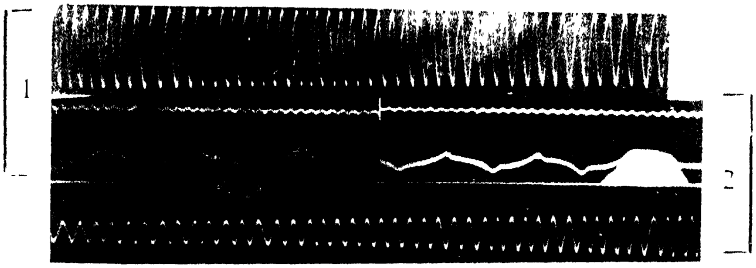


(b)

Hard hammer.



(c)



Different damping (Hard-pointed hammer)

(d)

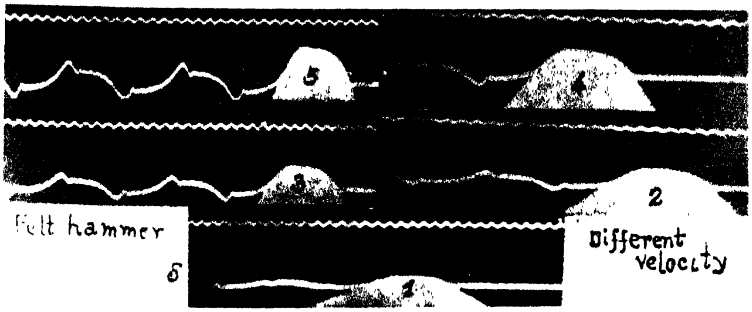


TABLE IV.

$$V = 45{\cdot}5\ \frac{\text{cm.}}{\text{sec.}},\ K = {\cdot}186,\ E = {\cdot}\infty$$

Radius in cm. of the head of the hammer.	$\phi \times 10^2$
Wedge shaped	3·0865
·635	3·1165
·852	3·1290
1·270	3·1330
1·587	3·1330
1·98	3·2011
2·222	3·3100
2·534	3·3490
3·200	3·3611
3·808	3·365

of damping is obtained in the usual way from the ratio of the amplitudes at the beginning and at a known interval of time. The string is made to have different damping by making the bridges yielding with the help of felt or cotton wool. The measurement of the duration of contact is done in the usual way for two different damping coefficients. It is found that the duration of contact does not change appreciably for the smaller values of damping coefficients. This is also obvious from the expression of duration of contact given by the Eq. (42), Phil. Mag., Vol. 12, p. 684. The results are given below and corresponding photograps are shown in Pl. XXVII,

TABLE V.

$V_0 = 45{\cdot}5$ cm/soc (Wedge shaped hammer)

$\phi \times 10^2 = 2{\cdot}997$ calculated for the hammer struck at mid-point when $K = 0$

Damping Coeff. (k).	Duration $\phi \times 10^2$
·186	3·0865
·535	3·0933

(F) In studying the effect of the velocity of impact in the case of the felt hammer striking at the mid-point, it is found that the duration of contact increases as the velocity of impact decreases. It is further found that the duration of contact (ϕ) multiplied by the fifth root of the velocity (V) of impact is constant, as is required by Hertz's theory of impact. Weak[4] as well Kaufmann[11] also have found experimentally that (ϕ) increases as V_0 decreases but they explained it as an experimental error. It is however significant that the relation cited above also explains their experimental data. The results are given in table (VI) and the corresponding curve in fig. (5) and the photographs in Pl. XXVII.

TABLE VI.

Kaufmann's Expt.

l—80 cm., $\frac{m'}{m}$ = ·376 a = 7·1 cms.

θ—11205

Velocity V Proportional to	ϕ/θ	$\phi V_0^{\frac{1}{5}}$
1·0	·95	$4·63 \times 10^{-3}$
1·6	·825	$4·92 \times 10^{-3}$
2·2	·82	$4·67 \times 10^{-3}$
3·8	·78	$5·09 \times 10^{-3}$
4·2	·79	$5·21 \times 10^{-3}$

Author's Expt.

l—600, m′/m—1·4

a—300, K—·186

Velocity of impact cm./sec.	$\phi \times 10^2$	$\phi V_0^{\frac{1}{5}}$
20·3	4·9190	$8·97 \times 10^{-2}$
45·5	4·0595	$8·71 \times 10^{-2}$
63·8	3·6025	$8·31 \times 10^{-2}$
87·0	3·4720	$8·47 \times 10^{-2}$
107·3	3·2955	$8·39 \times 10^{-2}$

Now the relation $\phi V_0^{\frac{1}{5}}=$constant suggests a modification which is to be introduced in the present theory, so that it may be applicable to the case of a felt hammer. This new effect it may be added was not known to George, Bhargav—Ghosh and other workers when they studied the case of the felt hammer

Further work in this line is in progress which will be published in due course.

I must conclude with my best thanks to Dr. K. C. Kar for his guidance and suggestions in the course of this work.

Physical Research Laboratory,
Presidency College,
Calcutta.

January, 1932.

Note added in proof :

I have attempted to show in the paper that the duration of contact (ϕ) varies inversely as $V_0^{\frac{1}{5}}$ where V_0 is the velocity of the hammer before impact. This is the well known Hertz's law of duration of contact for collision between two elastic balls. It is, however, highly doubtful whether Hertz's law will be valid even in the case of the pianoforte string, especially when it is remembered that according to the law the duration ought to be zero for large values of (V_0), whereas according to the standard experiments it has a definite value (ϕ_0). In a paper which is expected to be sent to the press shortly, the author has further extended his generalised theory of the pianoforte by taking into account the Hertz-effect. It is found from the theory that $(\phi-\phi_0)\propto\frac{1}{V_0}$. It is remarkable that this new law is also supported by the experiment.

(Sept., 1932.)

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29

Note on an Improved Form of an Induction Coil Buzzer.

By

H. Mukherjee.

(*Received for publication, 8th August, 1932.*)

Introduction.

Some years back the author undertook the measurement of resistances of some electrolytes. While proceeding with the work the necessity for an alternating current galvanometer was felt for accurate measurements. Accordingly, a galvanometer of the form of a vertical wattmeter was constructed.* It was then found that, in order to obtain the degree of accuracy which the galvanometer was capable of giving, a fairly large amount of alternating current was essential. Now the instruments generally used in laboratories, namely, the induction coil buzzers and microphone hummers, deliver a very small amount of current. The Vreeland oscillator and instruments of the type are the only sources known to the author which can give a sufficiently high current and which are, at the same time, fit for measurements of electrolytic resistances on account of their high frequencies of alternation; but the cost of such instruments is very high. As a cheap substitute for them, therefore, the instrument, described below, was conceived of. It gives a fairly large amount of alternating current of frequency 500 or more.

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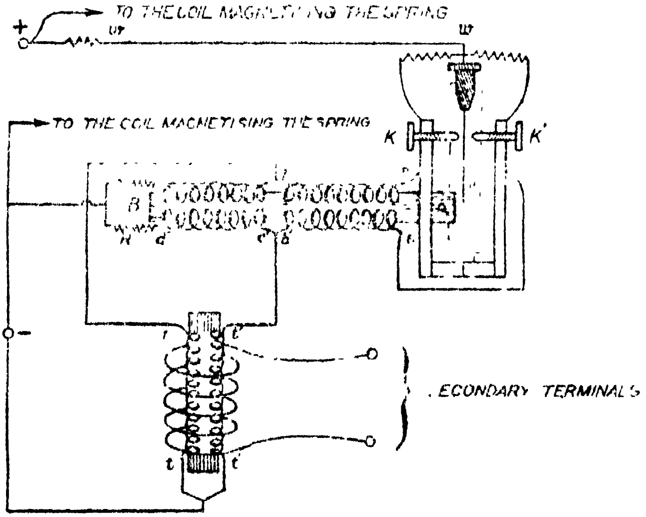
* H. Mukherjee, Eine Wechselstromgalvanometer, Zeit. f. Phys., **64**, 286, 1930; H. Mukherjee and S. S. Mukherjee, Eine neue Wechselstromgalvanometer, *ibid*, **67**, 702, 1931.

Description.

The instrument, of which the accompanying figure is a sketch, is essentially a combination of two buzzers and a closed-core transformer. The latter has been introduced to secure maximum efficiency of transformation. As the figure will show, the primary of the transformer is made up of a pair of coils (*tt* and *t't'*) having exactly the same number of turns. Similarly also the electromagnet (AA) which makes the spring V vibrate, is wound with pairs of coils *ab* and *a'b'* forming one pair and *cd* and *c'd'*, the other. The vibrator, which is attached to a firm iron support, is magnetised by a continuous current through a coil wound round the support and, as it touches the contact pieces, K and K' alternately during its vibration, current flows alternately through the elements constituting the coil pairs. The windings of these elements are such that current flows through them in opposite senses. Thus an alternating magnetic field is produced both in the transformer and in the electromagnet. The variation in the field of the transformer gives rise to the secondary current, while the alternation of polarity in the electromagnet maintains the vibration of the spring.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+
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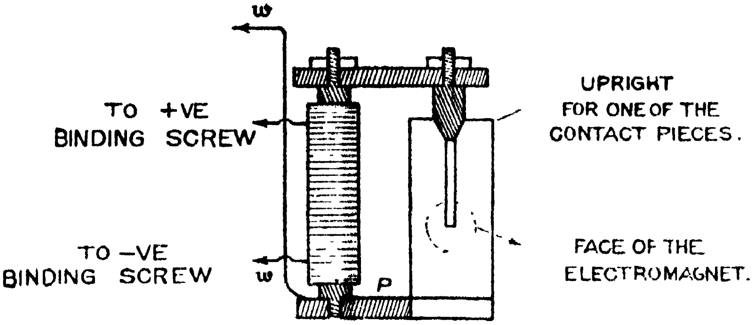
SECONDARY TERMINALS


w
TO +VE BINDING SCREW
TO –VE BINDING SCREW
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P
UPRIGHT FOR ONE OF THE CONTACT PIECES.
FACE OF THE ELECTROMAGNET.

FIG. (b)

In ordinary buzzers, which have only one contact piece, the decay of the current is more rapid than the growth and hence the 'break' electromotive force in the secondary is higher than the 'make' electromotive force. Consequently the intensity of the secondary current at 'break' is greater than that at 'make.' But, in the arrangement for double contact introduced in the instrument under discussion, there are both 'make' and 'break' at each contact and the change of magnetic field produced by the 'break' at one extremity is in the same direction as the growth of the field produced by the 'make' at the other. Therefore the effective secondary E. M. F. is the same in both directions. Moreover, in the arrangement for single contact, the vibrator vibrates with very nearly its natural frequency, but, in the arrangement for double contact, it is forced to vibrate with a frequency higher than its own.

As the vibration of the spring is forced, its frequency is very liable to change with the change in the magnitude of the impulse it obtains at each contact. Since, on closing the secondary circuit, the effective resistance and inductance of the primary of the transformer undergo a change, the current through the coils of the electromagnet and, consequently, the starting impulses obtained by the vibrator at the extreme positions are dependent on the secondary current whether the primary coils of the transformer are in series or in parallel with the corresponding coils of the electromagnet. To keep the frequency as constant as possible for all values of the secondary current, the series-parallel arrangement shown in the figure has been chosen. In this arrangement, the factors tending to diminish the field of the electromagnet are :

(*a*) The current induced by the secondary current in the inactive coil of the transformer ; this current, flowing through the inactive part of the set consisting of the coils *cd* and *c′d′* tends to produce an opposing field.

(*b*) The diminution in the current through the active part of the set *cd* and *c′d′* on account of the diminution in the inductance of the active part of the primary of the transformer caused by the flow of the secondary current.

The factor tending to increase the field is the extra current through the active part of the set *ab* and *a′b′* caused by the secondary current. The effects of the increase and the decrease in the field due to the above causes are made very nearly equal by adjusting the number of turns in the coils of the electromagnet and the values of the equal resistances R, R attached at the ends of the coils *cd* and *c′d′*. With a spring vibrator it is not possible to make the frequency absolutely invariable. But as the constancy of frequency is not essential for the measurement of electrolytic resistances, an adjustment for approximate constancy of the frequency is quite sufficient.

Greatest difficulty was experienced in removing the spark at each break. It has, however, been sufficiently diminished by tapering the ends of the contact pieces to fine points and placing two equal resistances in parallel with the gaps.

Specification of the Instrument constructed.

The oscillator constructed in this laboratory works with a two-volt accumulator. The frequency of the current obtained from it is about 650. The secondary E. M. F. is 5 volts and the maximum value of the secondary current is 100 milliamperes. The total input current including the current used to magnetise the spring is about 900 milliamperes. Thus the net efficiency of the apparatus is about 28 per cent.

If we leave the current of 500 milliamperes used to magnetise the spring out of consideration, the efficiency comes out to about 62 per cent. The amounts of error in measurements of resistances with this oscillator and a galvanometer of the wattmeter form are:—0·005 per cent. for 10 ohms, 0·01 per cent. for 100 ohms, 0·01 per cent. for 1000 ohms and 0·1 per cent. for 10,000 ohms. With a microphone hummer the errors are more than 10 times as much. The resistances measured were those of the coils of an ordinary post office box and could by no means be regarded as absolutely noninductive; still the balance points obtained were perfectly steady. Hence the oscillator can safely be used with ordinary resistance boxes, though the current from it is not sinuous.

Conclusion.

The present apparatus admits of further improvement. As it is, it is superior to an ordinary buzzer. It is inferior to a microphone hummer in that the current obtained from it is not sinuous. But, as will appear from the previous paragraph, a sinuous current is not essential if a galvanometer is used for measurements with alternating currents. The apparatus is not, however, suitable for measurements in which the constancy of the frequency of the current is necessary. For that purpose, a microphone hummer is a better instrument, though the frequency of the current from it also is, to a small extent, dependent on the secondary current. The best instrument for the purpose, however, would probably be one in which a tuning fork vibrates in front of the poles of an electromagnet and which does not contain a condenser as a part.

I am highly indebted to Professor S. N. Bose, but for whose sympathetic attitude and valuable suggestions the work could not be completed. My thanks are due also to my colleague Quazi Motahar Hossain who has helped me in adjusting the frequency of the apparatus.

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30

The Effect of the Indian Mountain Ranges on Air Motion

By

S. R. Savur.

(*Received for publication, 15th August, 1932.*)

In two papers[1 and 2] Dr. S. K. Banerji has discussed the effect of the Indian mountain ranges on the configuration of the isobars in India especially during the monsoon. In the course of the explanation he has brought in some new points which one finds it difficult to accept. These points are ;—

(1) Earth's rotation by itself is able to cause wind in the presence of barriers,

(2) The wind velocities and directions as observed by us are those with respect to axes instantaneously fixed in space,

(3) In steady air motion, the isobars coincide with the stream lines drawn with respect to instantaneously fixed axes.

These points will be discussed *seriatim.*

(1) *Earth's rotation by itself is able to cause wind in the presence of barriers.*

That this is the view put forward by Dr. Banerji (without proof) is clear from his two papers[1 and 2]; for example on p. 702 of (2) he says

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[1] S. K. Banerji, Ind. Jour. Phy., Vol. IV, Pt. VI, pp. 477-502.

[2] *Ibid,* Vol. V, Pt. VII, pp. 699-745.

"If then we wish to form a combined picture of stream lines in air, we must in the first instance form two separate pictures as follows :—

(1) * * *

(2) A picture of stream lines, which will be produced by the mountain barriers alone, assuming that the thermodynamical mechanism is absent, and the stream lines are due purely to the *relative motion introduced in the air on account of the presence of the barriers on the rotating earth.*" (Italics are mine.)

One may also infer this from the fact that the equations of motion due to the Field No. 1 (the thermodynamical mechanism) and Field No. 2 (due to rotation and mountain barriers) as given for example on pp. 495 and 496 of (1), are independent of each other.

This idea appears to be new to Meteorology, for in all the meteorological literature I have come across, the conception is that the motion of air is ultimately due to the difference in temperature between the various portions of the air, while the earth's rotation merely changes the direction of motion of the air. To quote only one authority in support of this, Humphreys says on p. 95 of his book[3] " Atmospheric circulation, whether manifesting itself in a monsoon, for instance, or in only a gentle lake breeze, is a gravitational phenomena induced and maintained by temperature differences."

Hence the idea that earth's rotation by itself produces wind in the presence of barriers is not acceptable.

(2) *The wind velocities and directions as observed by us are those with respect to axes instantaneously at rest in space.*

The following extract shows that the above is the view put forward by Dr. Banerji. On p. 717 of (2) we read: " Let us now suppose that we have a large number of wind vanes at

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[3] Humphreys :—Physics of the Air, 2nd Edition, 1929.

0·5 Km. *level* distributed all over India and that they are all read at a particular instant (say, 8 hrs.). Each observer reads the direction of the vane with reference to a pre-arranged axis, namely, the north-south line, and at that instant this line remains momentarily fixed in space. If now a series of stream lines be drawn from all these readings, these will be synoptic stream lines with refernce to instantaneously fixed axes."

This statement is not correct. The directions and wind speeds as observed by us can only be with respect to axes fixed in the earth. Again, the average wind velocities as observed by us do not exceed 30 miles per hour, whereas if they had been measured with respect to axes, instantaneously fixed in space, it can be easily shown that they would have been of the order of 800 miles per hour in our latitudes.

I consider this an important point because although the equations for stream lines given by Dr. Banerji are those with respect to axes instantaneously at rest in space, the values of U and V, the components of wind velocity, used in these equations appear to be of the order of 20 to 30 miles per hour, *i.e.*, those observed with respect to the earth. I do not see how this can be justified.

(3) *In steady air motion the isobars coincide with stream lines as drawn with respect to axes instantaneously at rest.*

No proof has been given in support of this except that the theoretical stream lines drawn by Dr. Banerji are very similar to the normal isobars in June (see Figs. 8 and 9 in (1)).

In regard to this agreement it has already been mentioned above that in drawing these stream lines wind velocities with respect to the earth appear to have been used instead of wind velocities with respect to axes instantaneously at rest. Hence if the correct values are used it is not known how far the shape of the stream lines will be modified.

Again, the equations for stream lines are those obtained by Stokes for the motion of a perfect fluid inside a closed sector (see p. 715 of (2)). It is not clear how these can be true in the case of air moving between two straight barriers meeting at a point, especially near the open ends of the barriers. They will hold much less in the case of air moving much further away, say in the Bay of Bengal. Besides, the values of the co-efficients in the equations have not been given either in (1) or (2). Hence it is not possible to say how far the stream lines shown in Fig. 8 of (1) represent the true stream lines drawn with respect to instantaneously fixed axes.

But there is still another objection. Col. Gold[4] has shown that the velocities *as observed by us* are very nearly tangential to the isobars. This has been confirmed by Lord Rayleigh[5] in a very elegant manner. This shows that the stream lines drawn with respect to the rotating earth coincide very approximately with the isobars. Hence the suggestions put forward by Dr. Banerji, *viz.*, that in steady air motion the isobars coincide with the stream lines drawn with respect to instantaneously fixed axes, cannot be accepted without further proof.

It is very possible that other readers may have difficulties similar to those mentioned above. Hence these have been put forward with the hope that Dr. Banerji may kindly clear them up.

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[4] E. Gold, Proc. Roy. Soc., Vol. 80A, 1908, pp. 436-443.

[5] Lord Rayleigh, Sc. Papers, Vol. VI, pp. 276-278.

31

Susceptibility of Liquid Mixtures with a New Apparatus

By

L. Sibaiya and H. S. Venkataramiah.

(Plates XXVIII and XXIX.)

(Received for publication, 2nd September, 1932.)

Abstract.

The diamagnetism of liquid mixtures has been investigated by weighing a pendant drop in a nonhomogeneous magnetic field. The variation in the time of formation of the drops is shown to affect the value of the susceptibility in the direction of enhancing the true deviation from the mixture law. The results obtained for pure liquids are however in good agreement with the accepted values.

The deviation of the susceptibility of the acetone-chloroform mixture from the mixture law has been studied with a new apparatus. A cylindrical glass test piece with the opposite quadrants ground off for obtaining high sensitiveness is suspended under the liquid at the lower end of a torsion fibre in a nonhomogeneous magnetic field. The twist due to the couple on the test piece being linearly related to the volume susceptibility of the surrounding liquid, the specific susceptibility has been determined with an error not exceeding one per cent. The observed maximum deviation of about 8% agrees well with the results of most observers. This deviation, which some investigators deny, is shown to be theoretically expected.

Introduction.

The magnetic susceptibilities of liquids and liquid mixtures have been recently studied by various observers, and the results obtained are not always concordant. This work was undertaken just after the publication of a paper by Trew and Spencer [1] on the susceptibilities of certain liquids and liquid mixtures. An improved method for weighing a pendant drop in a non-homogeneous magnetic field described in Part I, was employed for the susceptibility determinations; and our results were not in agreement with those of Trew and Spencer. While this work was in progress, Ranganadham [2] questioned the correctness of their values on the basis of results obtained by him using the capillary ascent method. Further contributions to the same subject were made by Van Aubel,[3] Hans Buchner,[4] Farquharson [5] and Ramachandra Rao and Sivaramakrishnan.[6] More recently Mathur and Kapur [7] published their results on magnetic rotations in liquid mixtures. The conclusions of these various investigators have been accepted as correct by Trew and Spencer [8] who attribute their results to "a mechanical defect in the arrangement for moving the magnet." Apart from the main controversy which ended by their note, the important question regarding the deviation of susceptibility values of liquid mixtures from the mixture law is still an open one. To mention a specific instance the acetone-chloroform mixture, shows a deviation from the mixture law according to Ranganadham and Hans Buchner, while Ramachandra Rao and Sivaramakrishnan report no deviation. Mathur and Kapur's values indicate a deviation, which however is not systematic. Exact information on this point might throw, as Stoner puts it, a valuable sidelight on the structure of the molecules

[1] Proc. Roy. Soc., 131, pp. 209-224, 1931 : also Nature 128, p. 152, 1931.

[2] Nature, 127, p. 975, 1931.

[3] Nature, 128, p. 455, 1931.

[4] Nature, 128, p. 301, 1931.

[5] Nature, 129, p. 25, 1932.

[6] Nature, 128, p. 872, 1931 : also Ind. Jour. Phys., VI, pp. 509-526, 1932.

[7] Ind. Jour. Phys., VII, pp. 15-18, 1932.

[8] Nature, 129, p. 95, 1932.

and the nature of the chemical combination. Our measurements on this mixture with a new apparatus, to be described in Part II, point definitely to a deviation from the mixture law and at the end of this paper theoretical considerations in support of this observation are given.

PART I.

*Susceptibility of Liquids by Pendant Drops.**

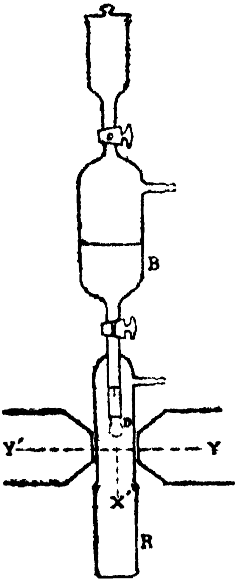

FIG. 1.

The method of forming a liquid drop at the end of a vertical glass tube in a non-homogeneous magnetic field for measuring the susceptibility of liquids was first employed by Abonnenc.[1] Adopting this method we have redesigned the apparatus in such a way as to prevent evaporation from the drops by forming them in a saturated space. Figure 1 gives a diagram of the apparatus used. The liquid or the liquid mixture in the bulb B flows slowly down the tube T and forms into a drop D at its end. The variation in the weight of the drop depends on whether it is formed above or below the line YY': in the case of a diamagnetic liquid an increase in weight is observed when the drop is formed above, and a decrease when formed below, YY', the magnitude of the variation depending on the position of the drop along XX.' The drop is slowly formed and after detachment it is received in the tube R. After collecting a known number of drops, the tube R is closed by a cap and the weight of the drops is determined. If the weight of a drop is found with and without the magnetic field the change in the weight is given by

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* Part I was read before the XIX Indian Science Congress, January, 1932.

[1] Comp. Ren., Vol. 190, pp. 1395-7. 1930.

$$\frac{\Delta m}{m} = \frac{1}{g}\left[\chi - \frac{k_a}{\rho}\right] H_y \frac{\partial H_y}{\partial x}$$

where χ represents the specific susceptibility of the liquid and ρ its density, m the mass of the drop with the magnetising field and Δm its variation when the field is removed. k_a is the volume susceptibility of the atmosphere surrounding the drop. The quantity $H_y \frac{\partial H_y}{\partial x}$ depends on the magnetising current, the disposition and the shape of the pole pieces, but does not alter so long as these are maintained steady. In all our experiments distilled water is used as the standard liquid and its specific susceptibility assumed as $-0{\cdot}72\times10^{-6}$. Hence if two liquids A and B are used:

$$\frac{\Delta m_A/m_A}{\Delta m_B/m_B} = \frac{\chi_A - \frac{k_a}{\rho_A}}{\chi_B - \frac{k_a}{\rho_B}} \text{ is approximately equal to } \frac{\chi_A}{\chi_B}\left[1 - \frac{k_a}{\rho_A\chi_A} + \frac{k_a}{\rho_B\chi_B}\right]$$

The magnetising current is kept steady at less than half the saturation value in order to prevent the heating of the electro-magnet. Though no special precaution is taken to maintain a steady temperature, the big bulk of the liquid in the bulb B is so far removed from the magnet and the dropping tube T is so well enclosed by a second glass tube that practically no variation of temperature was noticed. It is specially important to emphasise the fact that the drop must be formed very slowly for obtaining consistent results and therefore the prevention of evaporation of liquids is specially necessary. Mention however must be made of an inevitable source of error arising in the course of the experiment. The time of formation of a diamagnetic drop formed in the position indicated in Fig. 1 is found to increase when the magnetic field is put on. A separate experiment has conclusively indicated that the weight of a drop decreases as the time of its formation is increased. The expected increase in the weight of a drop due to the field is thus reduced on account of the increase in the time of formation. This cause always makes the value of the susceptibility obtained by this method to be less than the actual value by about 5%. The susceptibility of the liquid mixture also being less than the value calculated according to the mixture law in the binary mixtures we have here examined, the observed deviations are always in excess of the correct value. Hence a quantitative discussion of the variation from the mixture law is out of the question. Besides the correction term $\frac{k_a}{\rho}$ for the effect of the surrounding atmosphere is not quite determinate since the air is saturated with the vapours of the liquids used. But the mean values for the individual liquids compare favourably with the determinations by other observers :

	Pascal × 10^6	Trew and Spencer (Revised) × 10^6	Buchner × 10^6	Authors
Acetone	−0·581	−0·600	−0·580	−0 57 × 10^{-6}
Chloroform	−0·488	−0·510	−0 485	−0·46 × 10^{-6}
Acetic Acid	−0·55 (−0·58 G. Meslin)	...	...	−0·58 × 10^{-6}

Acetone-chloroform mixture.—Ranganadham [10] and Hans Buchner [4] obtained a maximum deviation from the mixture law amounting to 3% and 2% respectively : their observations are confirmed by the results of Farquharson.[5] Figure 2(*a*) shows our values for the liquid mixtures, and the deviation

Ind. Jour. Phys., Vol. VI, pp. 421-31, 1931.

maximum occurs at exactly the same percentage composition as recorded by the above observers. It is unfortunate that the correction note of Trew and Spencer [8] was received after the Fig. 2(*a*) was prepared; their results however show that the maximum deviation is observed by them at the same composition of the mixture. The figure shows also how the other physical properties like viscosity and vapour pressure [11] of the mixtures change with the relative proportions of the constituents and how they also exhibit the maximum deviation at about the same concentration. This maximum deviation occurs at 32% by weight of acetone, which corresponds to equal molecular concentrations of the two components. Besides it can be seen that maximum amount of heat is generated by mixing the two liquids in this proportion, thus pointing to the conclusion that a new substance is being formed, which some observers identify as dimethyl-trichloromethyl-carbinol.

Water-acetic acid mixture.—From experimental evidence based on Raman spectra Krishnamurti [12] has concluded that when 75% concentration of acetic acid is reached the Raman line present in pure acetic acid at 1667 cm^{-1} vanishes and a new line appears at 1712 cm^{-1}, which only becomes sharper with further dilution of the mixture with water. The stage at which the Raman line at 1667 cm^{-1} disappears, occurs at nearly equal molecular concentrations of the components and is perhaps attended with the formation of $CH_3COOH \cdot H_2O$. Then the line at 1667 cms^{-1} attributed to $C=O$ bond in the pure acid molecule vanishes. Dunstan and Thole's [13] viscosity measurements and our susceptibility measurements shown in Fig. 2 (*b*) also indicate a maximum variation at this concentration.

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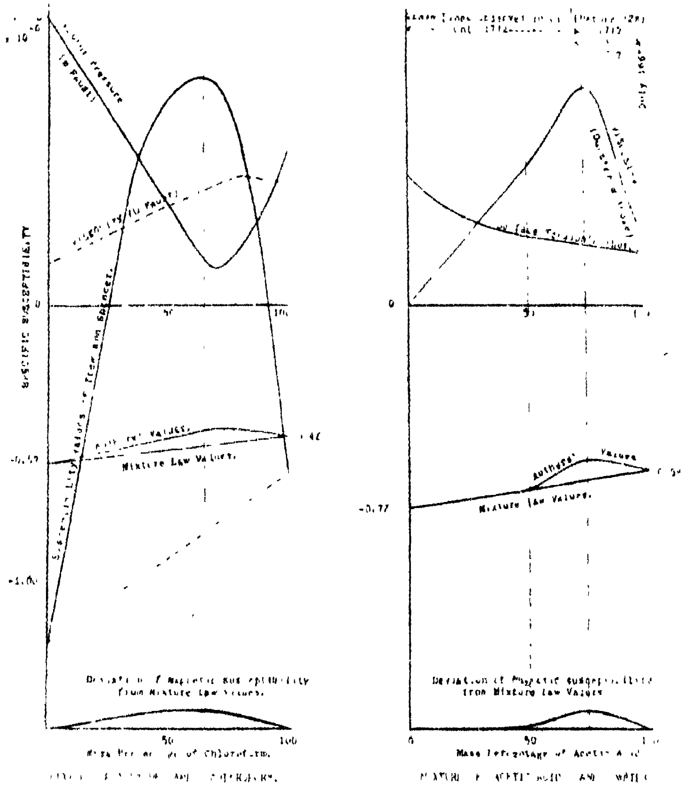
[11] C. Faust, Zeit. Physik. Chem., 79, p. 97, 1912.

[12] Nature, Vol. 128, p. 639, 1931.

[13] Jour. Chem. Soc., 95, p. 1556, 1909.


x 10^-6
Critical Pressure
SPECIFIC SUSCEPTIBILITY
Mixture Law Values.
0
50
100
-0.59
-1.00
Deviation of Magnetic Susceptibility from Mixture Law Values.
Mass Percentage of Chloroform.
Authors' Values
-0.77
Deviation of Magnetic Susceptibility from Mixture Law Values
Mass Percentage of Acetic Acid
MIXTURE OF ACETIC ACID AND WATER

(a)

(b)

Fig. 2

Percentage of acetic acid by weight	Observed value × 10^6	Calculated value, × 10^6	Differences × 10^6
100·0	−0·580	−0·580	0·000
90·0	−0·577	−0·594	−0·017
80·0	−0·565	−0·608	−0·043
70·0	−0·553	−0·622	−0·069
60·0	−0·629	−0·636	−0·007
50·0	−0·650	−0·650	0·000
10·0	−0·704	−0·706	−0·002
0·0	−0·720	−0·720	0·000

Miscellaneous Effects.—Mention may be made of a few interesting observations that we have noticed :—

1. Using the same liquid, say water, if the magnetising current in the electrc-magnet is varied, the form of the magnetisation curve is obtained by plotting the variation in the weight of a drop against the current. Since $\frac{\partial H_y}{\partial x}$ at any point depends mostly on the shape and the disposition of the pole pieces, Δm follows the variation of H_y, and the saturation current can be easily estimated when Δm attains a steady value (Fig. 3).

2. As the magnetising current is slowly increased from zero to the saturation value the time of formation of the drop gradually changes. Fig. 3 represents a set of typical values obtained for water drops formed in the position shown in Fig. 1. The magentic forces in this case tend to retard the formation of the drops. The effect of the time of formation on the weight of the drops and the consequent variation in the susceptibility values have been already discussed.

3. Since the weight of a drop without the field is determined for the liquid mixtures, a comparative estimate of the surface tension can also be made. Fig. 2 (*b*) gives the values for acetic acid-water mixture.

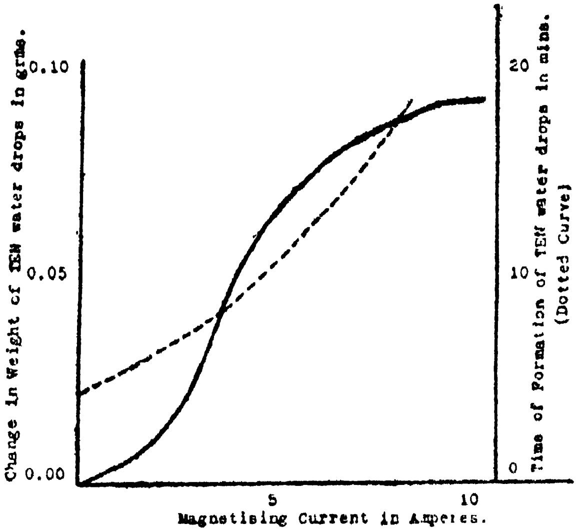


FIG. 3.

This pendant drop method of determining the susceptibility of liquids is a simple laboratory method and is just as easy in manipulation as the measurement of the surface tension by the drop method. Since the observation is affected by variations in the time of formation of the drop, it occurred to us that a new apparatus could be set up for the study of liquid susceptibilities on the lines first suggested by Wien for the study of gases.

PART II.

The test system of the new apparatus consists * of a pyrex or ordinary glass cylinder from which the opposite quadrants have been ground off. The grinding operation must be done carefully so as to obtain exact symmetry in the test piece, since any slight asymmetry would tilt it when immersed in a liquid. A thin glass stem fused to the test piece along its axis carries a plane mirror. The free end of the stem is attached to the lower end of a phosphorbronze suspension

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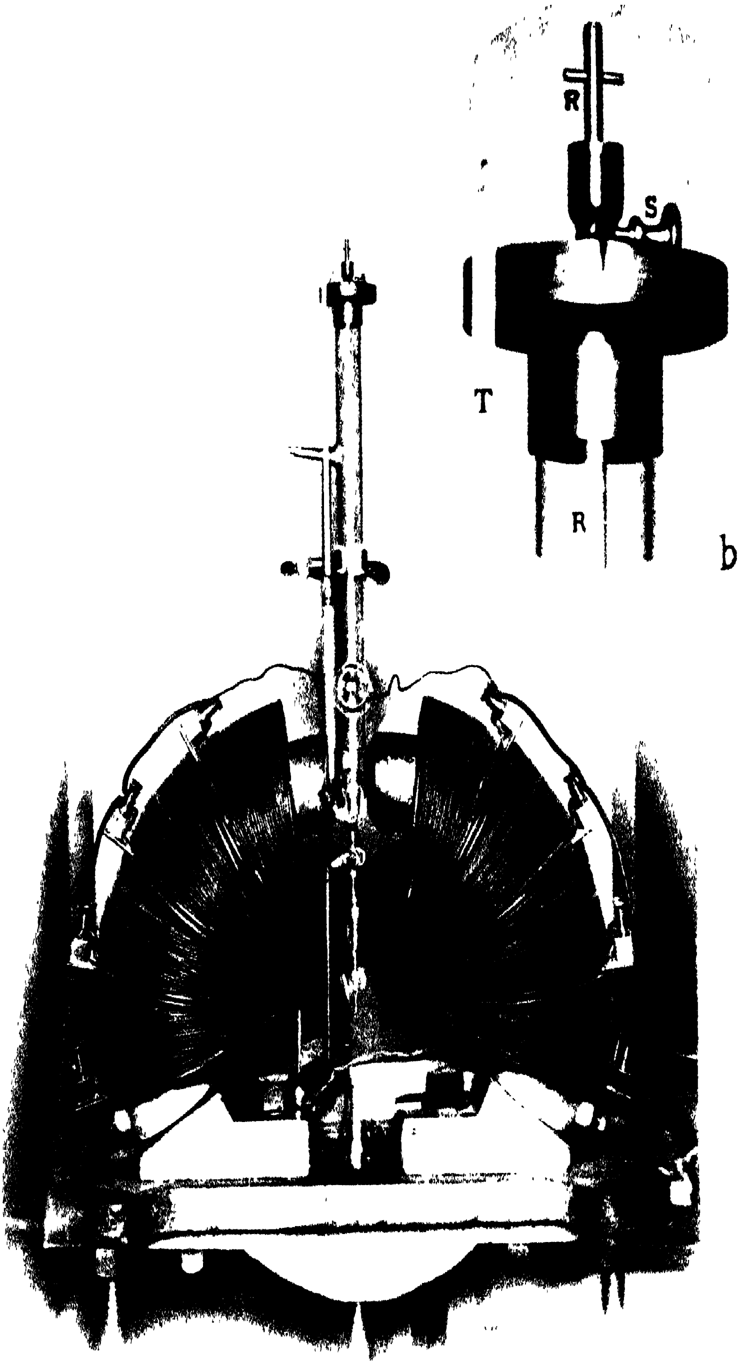
* A preliminary note regarding this apparatus has been published in 'Current Science,' Vol. 1, pp. 12-13, 1932.


R
S
T
R
b

(a quartz fibre is preferable), the upper end of which is soldered to a brass rod R [*vide* Fig. (*b*), Plate XXIX]. The rod is capable of vertical movement and can be fixed by a screw S in any desired position of the test piece with reference to the magnet. The test system and the suspension are encased in a wide glass tube (*vide* Fig. *a*, Plate XXIX) with an opening for cementing a lens in front of the plane mirror. The torsion head is fixed to the top of the glass tube. The liquid is inserted from a side tube, which in the course of the experiment is used for the insertion of a 1/10° thermometer T. The tap at the bottom of the tube serves to empty it after the completion of a set of readings. The disposition of the test piece with reference to the pole pieces is indicated in diagram 4.

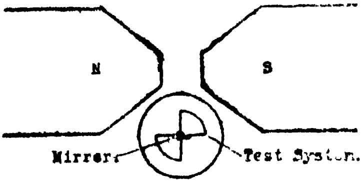


FIG. 4.

Methods of Manipulation and Calculation.—When the magnetic field is put on, the couple on the test piece twists the suspension, but the usual practice of turning the torsion head and bringing the test piece to the initial position and noting the twist has not been adopted as it is very trying. As an alternative, the test piece is adjusted to the zero position when the field is on (*vide* Fig. 4) and the resulting deflection when the field is removed is noted. Since the deflections and the positions in the close neighbourhood of the correct initial position of the test piece have been found to be linearly connected, the deflection in any particular position of the test piece could be estimated by interpolation with the neighbouring values. In order to attain high sensitiveness the reflecting mirror on the test piece is adjusted parallel to one of its ground faces which in its zero position is also parallel to the lines of magnetic force (Fig. 4). The relation between the deflections obtained when the magnetising current is switched off in any fixed position of the test piece in the field and the volume susceptibilities of the liquids is linear, thus rendering the calculation of volume susceptibilities simple. A density determination enables one to calculate the specific susceptibilities.

If the volume susceptibilities of the material of the test piece and the surrounding liquid be K_o and K respectively, the couple on the test-piece is

$$(K_o - K) \int \tfrac{1}{2} (\triangle H^2 \times r)\, dv$$

where *dv* is the volume element whose position vector relative to the axis of rotation is r and H, the field intensity at the point. If C is the couple per unit twist and θ the angular deflection,

$$K_o - K = - \frac{C\theta}{\int \frac{1}{2}(\Delta H^2 \times r) dv} = -\lambda\theta$$

Whence $K = K_o + \lambda\theta$

and it is thus clear that K and θ are linearly connected and that K_0 is obtainable by interpolation.

The performance of this new apparatus was tested by determining the susceptibilities of some pure liquids and it was found that the error of determination in no case exceeded one per cent. Two test pieces, one made of ordinary glass and the other of pyrex, have been separately tried but always with the same result. Incidentally it may be mentioned that the specific susceptibility of pyrex glass was found to be $-0{\cdot}298 \times 10^{-6}$ and that of ordinary glass used by us to be $-0{\cdot}356 \times 10^{-6}$. The investigation of the deviation of the susceptibility values of the acetone-chloroform mixture from the mixture law was next conducted with this apparatus. The following table shows the results obtained :—

Percentage of chloroform by weight	Observed value × 10^6	Calculated value × 10^6	Deviation × 10^6
0·0	−0·580	−0·580	0·0
21·2	−0·556	−0·564	−0·008
61·66	−0·518	−0·533	−0·015
72·25	−0·510	−0·526	−0·016
100	−0·505	−0·505	0·0

The maximum deviation from the mixture law values is about 3% which agrees well with the observations of Ranganadham, Hans Buchner and Farquharson. The variation is well outside the limits of experimental error and hence it is not possible to ignore this deviation.

In Part I, it has been pointed out that the vapour pressure and the viscosity of this mixture show deviations from the mixture law, the maximum deviation occurring as in the case of the magnetic susceptibility at nearly equimolecular proportions of the components. Also the magnetic rotations of this mixture have been found by Mathur and Kapur [7] to be different from the calculated values.

Generally when two liquids A and B are mixed together, the variation of any physical property from the mixture law is attributed to a chemical change resulting either in the formation of a new compound or in the dissociation of one or both the components. The former case, which corresponds to the mixture under discussion, can be represented thus :—

$$aA + bB \longrightarrow xA + yB + A_{a-x}B_{b-y}.$$

The susceptibility of the new compound $A_{a-x}\,B_{b-y}$ cannot in general be computed from the known values for A and B.

Applying Pascal's additive law, the calculation of the susceptibility of the new compound would entail the determination of a new additive constant, which bears no relation to the constants of the liquids A and B. Also in the case of a solution, Stoner mentions that the mixture relation does not invariably hold, for the state of the solute may vary with the concentration owing to the interaction with the solvent. Thus it follows that the deviation of the susceptibility of acetone-chloroform mixture from the mixture law should be real, consistent with the known facts regarding the variation of the other physical properties of this mixture. Combining these considerations with our experimental observations, we conclude that this mixture exhibits a deviation which at no concentration exceeds 3%.

UNIVERSITY OF MYSORE,
CENTRAL COLLEGE, BANGALORE.
15th August, 1932.

32

A Note on the General Spectrum of the Night Sky as observed in India.

By

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Solar Physics Observatory, Kodaikanal.

(Plate XXX.)

(Received for publication, 5th September, 1932.)

The presence of the green line 5577A due to neutral atomic oxygen may be considered to be established in the spectrum of the night sky in all parts of the world. But there is still considerable lack of knowledge regarding the general spectrum accompanying it. L. A. Sommer[1] from his examination of plates obtained at Gottingen, came to the conclusion that nitrogen bands are normally present in the night sky as in polar aurora, while Lord Rayleigh[2] has adduced strong reasons for the view that the spectrum of the normal night sky is essentially different from that of the polar aurora in as much as the former does not show the negative nitrogen bands which is a striking characteristic of the latter, and besides, shows two lines (or bands) which he calls X_1 and X_2 located at 4419 and 4168A. In a recent note, M. J. Dufay[3] has tabulated a large number of bands obtained in the spectrum of the western night sky taken in France: although some of the bands are common to the aurora and the night sky, the two cannot be considered as being identical.

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[1] L. A. Sommer, Z. Physik, Vol. 57, p. 582 (1929).

[2] Lord Rayleigh, Proc. Roy Soc.. A Vol. 131, p. 376 (1929).

[3] J. Dufay, Comptes Rhndus, Vol. 193, p. 1106 (1931).

In view of the general interest of the question and the non-agreement of views between different investigators a few long exposure photographs of the spectrum of the clear night sky were obtained at Poona (lat. 18° 30′) in February and March of this year. Owing to the low latitude, we may be fairly confident that the spectra will not be affected by even faint auroral discharges. Some comparative spectra of zodiacal light were also obtained.

The spectrograph used[4] had a single flint prism, the collimator having a focal length of 12 in. and aperture 1·5 in. and the camera having a Dallmeyer lens of focal length 2 inches and aperture ratio F/1·5. The dispersion of the instrument was such that the distance between the green line 5577A and the H line of the solar spectrum on the plate was about 3·5 mm. The plates used were Extrema-Ortho or Finogran manufactured by the Mimosa A.G. of Dresden. This has a region of high sensitivity from 5400-5750 and 4800-3900 A.U. A good spectrum was obtained with an exposure of 25½ hours on five nights on clear moonless skies between the 11th and 15th February. The exposures were made with the collimator facing south-west at an angle of 25° with the horizon and the slit-width was 0·67 mm. As all the exposures were after 22 hs. 30 m., the spectrum would not be affected by the zodiacal light. Another good plate was obtained between the dates 28th February and 5th March with a slit of 0·47 mm., the total time of exposure being 36¾ hrs. For showing the lines or bands more distinctly in print, Fig. 1 was obtained by superposing the two long exposure night sky spectra and making an enlargement. The close

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[4] K. R. Ramanathan, 'Nature,' February 20 (1932).

Fig. 1. Night sky spectrum, effective exposure 62 hrs.

(a)

Night sky spectrum

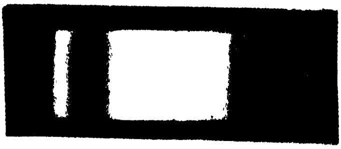
Slit 0·67 mm., exp. 25½ hrs.

Fig. 2. (b)

Zodiacal light and night sky.

Slit 0·67 mm., total exp. 10 hrs.

(c)



Twilight sky.

Slit 0·27 mm., 51 to 36 min. before sunrise.

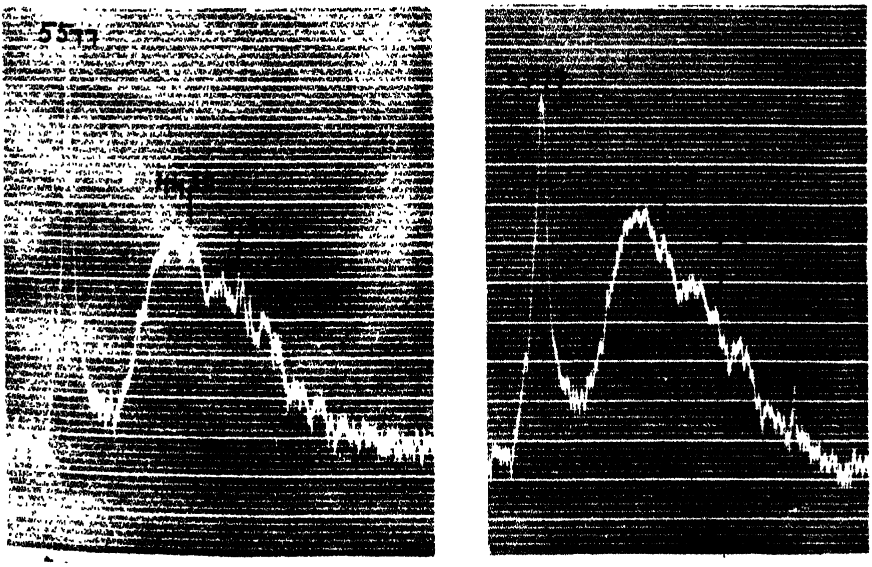


Fig. 3. Microphotograms of night sky spectra.

(a) Slit 0·47 mm., exp. 36¾ hrs.

(b) Same as fig. 2 (a).

resemblance of this night sky spectrum with that obtained by Slipher (and reproduced in Lord Rayleigh's paper) shows that the occurrence of the general spectrum in the non-polar aurora is as much a world-wide phenomenon as that of the more conspicuous green line and is quite distinct from the polar aurora. The bright lines or bands referred to by Lord Rayleigh as X_1 and X_2 are marked in the figure. In order to convey an idea of the relative intensities of the bands, microphotometric traces of the plates are shown in Figs. 3(*a*) and 3(*b*).

The following table gives the approximate wave-lengths of the more conspicuous of the lines or bands as measured from these plates. The wave-lengths are calculated by using Hartmann's formula, the constants being determined from the measurements of the positions of hydrogen and helium lines in a comparison spectrum, and the known wave-length 5577A being made use of to go over from one spectrum to the other. Other plates with still shorter exposures also show some of these bands and wave-lengths obtained from them agree within the accuracy of measurement with those obtained from these two plates.

There are many other lines listed by Sommer and Dufay but, with the limited range of sensitiveness of the Mimosa plate and the low dispersion employed, more lines could not be definitely identified in my plates.

It is interesting in this connection to recall the old observations of Mr. E. A. Fath[5] on the integrated spectrum of the Milky Way who, with an exposure of 65 hs. 13 m., obtained a spectrum which showed a bright line at 416$\mu\mu$ and "faint additional absorption lines at 411, 421 and 448$\mu\mu$." He also noted that the line G was very broad. From his description of the spectrum and its reproduction in the paper, it shows great resemblance to the spectrum of the night sky. As both Fath

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[5] E. A. Fath, 'Astrophys. Jour.' Vol. 36, p. 362 (1912).

TABLE I.

Positions of Lines or Bands in the Night Sky Spectrum.

	1	2	3	4	5
	Observed at Poona	Observed by Lord Rayleigh	Observed by Sommer	Observed by Dufay	Observed by Slipher in the Zodiacal light
1	5577A	5577	5577	5577	5577
2	4555	—	4552	4554	—
3	4430	4419	4457 4122	4449 4422	4424
4	4270		4270	4268	4280
5	4180	4168	4166	4171	4175
6	4090		—		4080
7	4040		—	4044	—
8	3960		3976 3946	3984 3951	 —
9			3916	3914	3916

and Lord Rayleigh have assumed, it is possible that there is a background of continuous spectrum with the Fraunhofer lines on them. In that case the last of the "lines" in the above table would correspond to the bright region between the H and X lines and the last "gap" to the K line, but with the low dispersions so far employed we cannot be very certain about the identity of the lines. Kaplan[6] has suggested that X_1 and X_2 are emitted by singly ionized oxygen atoms with wave-lengths 4416·97 and 4169·23A, but the reason why these two lines should be selected is not at all evident. While there seems to be little doubt that 4275 and 3916 are to be identified with negative nitrogen-band heads, the securing of better resolved spectra of the night sky and a more precise determination of the wave-lengths involved are necessary preliminaries to tracing the origin of the lines.

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[6] J. Kaplan, Phys Rev., Vol. 38, p. 1048 (1931).

There is nothing to indicate that the nights should be exceptionally bright in order to show the general spectrum other than the green line. Whenever sufficient exposure has been given, the spectrum has come out with similar characteristics. The relative intensities of the bands do not however remain constant. This can well be seen by comparing the microphotograms in Figs. 3 and 4. The wave-lengths 4130 and 4180 are comparatively weaker in Fig. 4. As Lord Rayleigh has pointed out, some exceptionally bright nights do occur. For instance, a four-hour exposure on the night of 11-4-31 from the roof of the Indian Association for the Cultivation of Science at Calcutta brought out the bands more clearly than many exposures of much longer duration.

In order to show the difference between spectra of the zodiacal light, the light of the night sky and the twilight sky, photographs of these are given in Fig. 2. Fig. 2 (*b*) is really a composite of zodiacal light and night sky, the exposures being towards the west sky from the end of evening twilight to midnight and towards the east from midnight to moonrise, the total time of exposure being 10 hours. The intensity of the zodiacal light falls off rapidly on the shorter wave-length side of 4400A. The Fraunhofer lines G and H can be identified in it and the line 5577A comes out strong. Some of the other peaks of intensity in it correspond to bands in the night sky spectrum, but it requires further study to say whether these are due to the background of the night sky or are characteristic of the zodiacal light. Slipher[7] has recently reported the finding of emission lines or bands near 5577A, 4424A, 4280A, 4175A, 4080A and 3916A in the spectrum of the zodiacal light. It will be seen from Table I that the first five of these agree within the accuracy of measurement with the bands listed in Table I.

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[7] V. M. Slipher, Lowell Obs Circ. February 20 (1931), reported in Popular Astronomy, Vol. 40, p. 439 (1932).

My thanks are due to Mr. S. P. Venkateswaran, M.A., for his kind help in constructing the spectrograph.

33

The Effect of the Indian Mountain Ranges on Air Motion.

BY

S. K. BANERJI.

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It is clear from the three points which Dr. S. R. Savur has raised in the preceding note[1] that he is labouring under certain fundamental misconceptions.

(1) The question whether earth's rotation by itself is able to cause wind in the presence of barriers does not at all arise in the problem which I have discussed in the two papers to which he refers. There is wind produced by *thermo-dynamical mechanism* and in the path of this wind we interpose certain mountain barriers. Surely the original circulation will be profoundly modified by the barriers. The wind produced by thermodynamical mechanism is represented by the stream function ψ_1 (Field No. 1) and the effect of the mountain barriers on this wind by ψ_2 (Field No. 2). The function ψ_2 must satisfy certain boundary conditions on the barriers, which *rotate* with the earth, as explained on pp. 712-13 of paper (2), and when ψ_2 is determined, the modified circulation is given by $\psi_1+\psi_2$. Immediately after giving an approximate physical interpretation of Field No. 1 and Field No. 2 by means of the two pictures mentioned on p. 702 of

[1] Page 389 of this issue.

paper (2), which Dr. Savur quotes, I state on the same page as follows: "Since Field No. 1 rspresents the primary current and Field No. 2 the disturbance due to the boundaries, a good approximation will be obtained of the combined field if these component fields are compounded together. *When, however, a closer approximation is desired it will be necessary to calculate the smaller order terms involving the mutual action of these two fields.*" Any one who is familiar with the solution of the boundary problems in mathematical physics by the method of successive approximations will find no difficulty in understanding the meaning of the statement. This statement makes it perfectly clear, without any kind of ambiguity, that an approximate solution is obtained only when the two fields are compounded together and that therefore the two fields must be co-existent. The existence of Field No. 2 in the absence of Field No. 1 is not at all contemplated. The remark of Dr. Savur that in the examples on pp. 495 and 496 of (1) Field No. 1 and Field No. 2 are independent of each other is misleading. In the footnote on p. 496 of (1) and on p. 713 of (2) it is clearly stated that in obtaining the solution the most general expression for ψ_2 has been assumed. In the examples only the most important terms have been retained. The constants involved in the expression for ψ_2 are functions of the constants in ψ_1. The two fields are therefore not independent of each other.

The method of determining the constants is the one usually employed in boundary problems of this kind and consequently details were not given in my papers. I will, however, briefly indicate the steps here in order to make my points clear. Let us consider the corner over Bengal bounded by the Himalayan Range[2] and the Burma Hills, each supposed to be of equal length a. If we use polar co-ordinates (r, θ) then the Burma Hills will have the equation $r=0$ to a, $\theta=\alpha$, and the Himalayan range $r=0$ to a, $\theta=\beta$. If the centre of the 'Low' due to thermodynamical mechanism be taken at $r=c$, $\theta=\gamma$, then

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[2] The Himalayan Range is longer than the Burma Hills, but we consider here only the portion equal to the length of the Burma Hills as forming the northern boundary of the corner.

$$\psi_1 = \mathrm{V} \log \{r^2 - 2rc \cos(\theta-\gamma) + c^2\}^{\frac{1}{2}} \qquad \ldots \quad (1)$$

[see pp. 729-32 of (2)].

Expanding by Fourier's theorem, we get

$$\psi_1 = \mathrm{V} \log c + \mathrm{V}\left[-\frac{r}{c} \cos(\theta-\gamma) - \frac{1}{2}\frac{r^2}{c^2} \cos 2(\theta-\gamma) - \frac{1}{3}\frac{r^3}{c^3} \cos 3(\theta-\gamma) - \ldots \right]$$

$$r \angle c. \qquad \ldots \quad (2)$$

For Field No. 2, we assume the most general expression

$$\psi_2 = (\mathrm{A}_1 \cos\theta + \mathrm{B}_1 \sin\theta)\frac{r}{a} + (\mathrm{A}_2 \cos 2\theta + \mathrm{B}_2 \sin 2\theta)\frac{r^2}{a^2}$$

$$+ (\mathrm{A}_3 \cos 3\theta + \mathrm{B}_3 \sin 3\theta)\frac{r^3}{a^3} + \text{etc.} \qquad \ldots \quad (3)$$

If λ is the mean latitude over Bengal, then the boundary condition over the barriers becomes

$$\frac{\partial}{\partial r}(\psi_1 + \psi_2) = \omega r \sin\lambda, \qquad \ldots \quad (4)$$

for $r=0$ to a, $\theta=\alpha$, and also for $r=0$ to a, $\theta=\beta$ [see p. 712 of (2)].

We substitute the expressions (2) and (3) in this equation, differentiate with respect to r, and then put $\theta=\alpha$. We thus get an equation which holds for all values of r from 0 to a. We therefore equate the co-efficients of different powers of r on either side. In a similar way we put $\theta=\beta$ in equation (4) and equate the co-efficients of different powers of r on either side. We thus get from the boundary conditions

$$\frac{A_1}{a} = \frac{V}{c}\cos\gamma\ , \qquad \frac{B_1}{a} = \frac{V}{c}\sin\gamma \tag{5}$$

$$\left.\begin{aligned} \frac{2A_2}{a^2}\cos 2\alpha + \frac{2B_2}{a^2}\sin 2\alpha - \frac{V}{c^2}\cos 2\,(\alpha-\gamma) &= \omega\sin\lambda \\ \frac{2A_2}{a^2}\cos 2\beta + \frac{2B_2}{a^2}\sin 2\beta - \frac{V}{c^2}\cos 2\,(\beta-\gamma) &= \omega\sin\lambda \end{aligned}\right\} \tag{6}$$

$$\left.\begin{aligned} \frac{3A_3}{a^3}\cos 3\alpha + \frac{3B_3}{a^3}\sin 3\alpha - \frac{V}{c^3}\cos 3\,(\alpha-\gamma) &= 0 \\ \frac{3A_3}{a^3}\cos 3\beta + \frac{3B_3}{a^3}\sin 3\beta - \frac{V}{c^3}\cos 3\,(\beta-\gamma) &= 0 \end{aligned}\right\} \tag{7}$$

etc. etc.

The pairs of equations bracketed give the values of A_2, B_2, A_3, B_3, etc. It will be clear from the above equations that the constants determining Field No. 2 depend on V, c and γ, that is, on Field No. 1. The two fields are therefore clearly not independent of each other.

The centre of the 'Low' is at a considerable distance away from the corner over Bengal. Consequently c is very large compared with the dimensions $(a \times a)$ of the field over Bengal. In the expansion (2) of ψ_1 we can neglect all terms involving cubes and higher powers of $1/c$. When this approximation is made, A_1, B_1, and A_2, B_2 are given by (5) and (6), but the remaining equations reduce to

$$A_3 = 0, \quad B_3 = 0, \quad A_4 = 0, \quad B_4 = 0, \text{ etc.}$$

Field No. 2 has therefore the form

$$\psi_2 = \frac{V}{c}\cos\gamma .\, x + \frac{V}{c}\sin\gamma .\, y + \frac{A_2}{a^2}(x^2 - y^2) + \frac{2B_2}{a^2}xy \tag{8}$$

where A_2 and B_2 are given by equations (6). This is precisely the expression which has been used in my papers. If in the expression for ψ_1, we neglect also the terms involving $1/c^2$, then we see from (6) that A_2 and B_2 depend only on $\omega \sin \lambda$ and the angles defining the corner. In other words, the constants A_2, B_2 depend purely on the rotation of the corner. It is thus seen that the most important contribution to the expression ψ_2 comes from this source. It is clear from the above derivation that the expression for ψ_2 holds over a circular field of radius a with the corner at its centre.

When we neglect squares and higher powers of $1/c$, we have close to the barriers

$$\psi_1+\psi_2=\mathrm{V}\log r+\frac{\mathrm{A}_2}{a^2}(x^2-y^2)+\frac{2\mathrm{B}_2}{a^2}xy. \tag{9}$$

In other words, close to the barriers Field No. 2, as defined on p. 495 of paper (1) or p. 702 of (2), and which Dr. Savur quotes, preponderates. Outside the circular field of radius a defined above, we have to use "external harmonics" in the expression for ψ_2. Away from the barriers, therefore, ψ_2 has, owing to the law of continuity, the form

$$\psi_2=(\mathrm{A}_1\cos\theta+\mathrm{B}_1\sin\theta)\frac{a}{r}+(\mathrm{A}_2\cos 2\theta+\mathrm{B}_2\sin 2\theta)\frac{a^2}{r^2}+\text{etc.} \tag{10}$$

where A_1, B_1, A_2, B_2, etc., have the same values as above. As a consequence of the inverse powers of r, ψ_2 rapidly diminishes in importance with increasing distance away from the barriers. But the form of ψ_1 remains the same as in (1) or (2). Consequently away from the barriers, ψ_1 preponderates.

When a fresh mass of air enters into the partially closed space included between mountain barriers, hydrodynamics tells us that relative motion must ensue purely as a consequence of the rotation of the frame containing the barriers. The case in which the same mass of air remains rotating for ever inside a steadily rotating frame is purely of academic interest and does not occur in the atmosphere. In consequence of the thermodynamical mechanism the mass of air in any partially bounded space is being continually renewed. I clearly state on p. 702 of paper (2): "It need hardly be mentioned that in nature we can never visualise Field No. 2. For, nowhere can the thermodynamical mechanism be absent." Whether in the case when the same mass of air remains rotating for ever, it will, owing to viscosity, rotate after a sufficient length of time as a solid body, does not appear to have been definitely solved. The best answer to the question has been given by Lord Rayleigh in his paper "On the motion of a viscous fluid," Phil. Mag., Vol. XXVI, pp. 776-86, 1913 [Scientific Papers, Vol. VI, pp. 187-96. The dissipation function has to be a minimum and rotation as a solid body is a final possible state. But whether the dissipation function can be minimum under some other state we do not know. When the second order terms in the dynamical equations cannot be neglected, we have practically no knowledge on the subject. We are, however, not concerned with the question in the problems discussed in my papers.

The quotation made by Dr. Savur from Humphreys' 'Physics of the Air' does in no way suggest that atmospheric circulation should undergo no distortion when it strikes against mountains.

(2) The remark that my view is that "the wind velocities and directions as observed by us are those with respect to axes instantaneously at rest in space" is a pure mis-representation. The quotation made from p. 717 of paper (2) in support of the remark refers to observations of *wind directions only* (not velocities) *made at the same instant* (synoptic) at a close network of stations over India. The quotation specifically mentions merely *wind-vanes*, but Dr. Savur brings in both *velocities and directions*. It is surprising that he does not know that wind vanes record directions only and *not velocities*. For the

tracing of stream lines, the knowledge of wind directions at a close net-work of stations is sufficient; we do not require to know the velocities. Furthermore it has been strongly emphasised in italics on p. 704 of (2) that the whole discussion is based on the assumption of a "steady circulation"—a steady monsoon current. The observations with wind vanes referred to are not the ordinary observations but synoptic observations under *steady circulation.* Emphasis must therefore be laid on two facts that the direction of the wind vane with reference to the N-S line (fixed on the earth) at any station does not change with time, and (2) that the readings of the wind vanes at all the stations are taken not only *instantaneously* but also at the *same instant.* As a consequence of the first condition the direction of wind becomes purely a geometrical angle, which at a station remains constant for all time. It no doubt varies from station to station but depends merely on the co-ordinates of the station and not on the time. The stream lines with reference to the N-S line fixed on the earth are therefore a series of geometrical curves which do not change their form with time and may therefore be regarded as fixed to the earth itself. With reference to the axes fixed on the earth these curves consequently represent not only the stream lines but also the paths of the particles. Now suppose that a line fixed in space coincides with the N-S line fixed on the earth at a particular instant. Since the two lines coincide, all readings of angles giving the directions of wind *instantaneously* taken will be the same whichever of the two axes they refer to. Consequently the instantaneous stream lines with reference to the axis fixed in space are the same as those drawn with reference to the N-S line fixed on the earth.[3] This relationship is a pure consequence of the fact that the velocities as well as the stream function are functions of coordinates only and not of the time. With reference to axes fixed in space we can have two distinct stream functions ψ and ψ'. The function ψ which represents the instantaneous stream lines at any instant does not determine the paths of particles. Since the circulation is steady and since the earth's angular velocity is constant, we will, if we determine the resultant motion at any point due to relative velocity and earth's rotation obviously find that its direction with reference to axes fixed in space does not change with time. By plotting these directions of the resultant motion at all the stations we will get a new set of stream lines denoted by $\psi' =$ constant, which will remain the same with reference to the axes fixed in space for all time. The stream lines $\psi' =$ constant will therefore represent the paths of the particles with reference to axes fixed in space. We thus see that instantaneous stream lines are not the paths of particles with reference to axes fixed in space. But with reference to axes fixed on the earth, the paths of particles and instantaneous stream lines are the same.

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[3] The best way of realising this is to consider that the stream lines with reference to the N-S line fixed on the earth are permanently *engraved* on the surface of the earth. If we take an *instantaneous* view from a point fixed in space and above the surface, we will see the engraved lines exactly as they are. Suppose for clearness that one stream line coin-

These inferences can be readily drawn from the dynamical equations. Furthermore, the values of U and V used in my papers are the observed wind velocities because all the dynamical equations have been expressed in terms of relative velocities. There is nothing to prevent us referring our dynamical equations to momentarily fixed axes and at the same time expressing them in terms of "relative velocities" and the angular velocity of the earth, which is a constant. Most of the difficulties of Dr. Savur appear to me to be due to his failure to recognize this fact. The remarks in the second and

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cides with the boundary walls of the Meteorological office at Poona and we take an instantaneous photograph from a point fixed in space above the compound. We would get the same picture as we would obtain if we exposed the camera in the same way from a point above the compound but fixed to the earth.

third paragraphs of his art. 2 are due to his illusion that if the dynamical equations refer to fixed axes then the components of velocities in which they are expressed must necessarily refer to fixed axes. His so-called "important point" would appear to be no point at all. Let us refer the equations of motion of the fluid covering the rotating earth to a set of axes passing through the centre of the earth and instantaneously fixed in space. The polar axis is a fixed axis. Let θ and ϕ be the co-latitude and longitude respectively of any point in the atmosphere and z its altitude measured outwards along a normal and let ω be the earth's angular velocity. The kinetic energy of unit mass is given by

$$2\,T=(R+z)^2\dot{\theta}^2+\varpi^2(\omega+\dot{\phi})^2+\dot{z}^2, \tag{11}$$

where R is the radius of curvature of the meridian section of the surface of reference (very nearly equal to earth's radius) and ϖ the distance of the particle from the polar axis.

The above expression represents the absolute kinetic energy with reference to axes fixed in space and *not* the relative kinetic energy with reference to axes rotating with the earth. This is so because the angular velocity $\dot{\theta}$ is measured from the polar axis which is fixed in space, and $\omega+\dot{\phi}$ is measured with reference to a meridian, which is also fixed in space, and $\dot{z}$ from a fixed level surface.

By using Lagrange's formula, we get the equations of motion[4] in the form

$$\frac{Du}{Dt}-2\,\omega v\,\cos\theta=-\frac{1}{R+z}\,\frac{\partial P}{\partial\theta}, \qquad \ldots \tag{12}$$

$$\frac{Dv}{Dt}+2\,\omega\,u\,\cos\theta+2\,\omega\,w\,\sin\theta=-\frac{1}{\varpi}\,\frac{\partial P}{\partial\phi}, \qquad \ldots \tag{13}$$

$$\frac{Dw}{Dt}-2\,\omega v\,\sin\theta=-\frac{\partial P}{\partial z}, \qquad \ldots \tag{14}$$

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[4] Lamb's Hydrodynamics, 4th Edition, pp. 318-20 ; Jeffreys, "On the dynamics of wind," Quart. Journ. Roy. Met. Soc., Vol. 48, p. 29 (1922).

where u, v, w are the components of relative velocity in the north-south, east-west and vertical directions and are given by

$$u=(\mathrm{R}+z)\dot{\theta}, \quad v=\varpi\dot{\phi}, \quad \mathrm{W}=\dot{z}, \qquad \ldots \quad (15)$$

and

$$\frac{\mathrm{D}}{\mathrm{D}t}=\frac{\partial}{\partial t}+\frac{u}{\mathrm{R}+z}\frac{\partial}{\partial \theta}+\frac{v}{\varpi}\frac{\partial}{\partial \phi}+\frac{\partial}{\partial z}, \qquad \ldots \quad (16)$$

$$\frac{p}{\rho}=\mathrm{P}-\Omega+\frac{1}{2}\,\omega^2\varpi^2, \qquad \ldots \quad (17)$$

p is the pressure and Ω is the gravitational potential due to the earth's attraction.

Because equations (12), (13), (14) have been derived from absolute kinetic energy with reference to fixed axes, they clearly refer to the instantaneous positions of the axes of θ, ϕ and z. (The axis of θ and the reference surface for z are, of course, definitely fixed so far as the diurnal rotation is concerned). $u/(\mathrm{R}+z)$ is extremely small, and so also v/ϖ, except near the poles. If we neglect vertical motion, which is always small, we see from (16) that

$$\frac{\mathrm{D}}{\mathrm{D}t}=\frac{\partial}{\partial t},$$

But for steady motion $\dfrac{\partial}{\partial t}=0$.

Therefore, equations (12) and (13) become

$$-2\,\omega v\cos\theta=-\frac{1}{\mathrm{R}}\frac{\partial \mathrm{P}}{\partial \theta}, \qquad \ldots \quad (18)$$

$$2\,\omega\, u\cos\theta=-\frac{1}{\varpi}\frac{\partial \mathrm{P}}{\partial \phi}. \qquad \ldots \quad (19)$$

Writing $Rd\theta = dx$ and $\varpi d\phi = R \sin\theta\, d\phi = dy$, we get

$$-2\omega v \cos\theta = -\frac{\partial P}{\partial x} \qquad \ldots \quad (20)$$

$$2\omega u \cos\theta = \frac{\partial P}{\partial y} \qquad \ldots \quad (21)$$

In making the above deductions, we have *not* changed the axes from their instantaneously fixed positions in space, with which we started, to rotating axes. Equations (20) and (21), just like equations (12) and (13), refer therefore to axes instantaneously fixed in space. These equations could have been deduced by merely considering the steady rotation of a small area with angular velocity $\omega \cos\theta$ about a vertical axis.

Equations (20) and (21) are exactly the same as those given under (5) on p. 706 of paper (2) with the omission of the frictional terms. At the bottom of p. 705 of (2), it has been definitely stated that these equations refer to instantaneously fixed axes.

It should be noticed that although the dynamical equations (20) and (21) refer to fixed axes, the components of velocity u, v entering into them are the "relative velocities" and not the absolute velocities. For a steady circulation, we can neglect the variation of density of air at any point with time. The equation of continuity[5] in the above co-ordinates therefore becomes

$$\frac{1}{\varpi}\frac{\partial(\varpi u)}{R\partial\theta} + \frac{1}{\varpi}\frac{\partial v}{\partial\phi} = 0. \qquad (22)$$

Since $\frac{\partial\varpi}{R\partial\theta} = \cos\theta$ and $u\cos\theta/\varpi$ is extremely small, the above equation on putting, as before, $Rd\theta = dx$, $\varpi d\phi = dy$, reduces to

$$\frac{\partial u}{\partial x} \quad \frac{\partial v}{\partial y} = 0 \qquad (23)$$

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[5] Lamb's Hydrodynamics, 4th Edition, p. 320 and also p. 294.

The stream function ψ, being orthogonal to the velocity potential, would as a consequence of the above equation satisfy

$$\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}=0. \qquad \ldots \quad (24)$$

Since u, v are the relative velocities, ψ is the relative stream function. It is thus clear that when we make the approximation as explained above, the relative stream function for steady motion satisfies the same equation whether the axes are instantaneously fixed in space or rotate with the earth. In my paper the solutions of the above equations have been used. They are therefore expressed in terms of the relative velocities. This is precisely the reason why in the numerical computation, the observed values of wind velocities have been used.

We draw our synoptic weather maps on a plane surface, that is to say, on a plane either parallel to or passing through the polar axis. The equations (20) and (21) being two—dimensional do conform to such plane representation. The velocity u then is measured along the polar axis and v perpendicular to the polar axis. The direction of wind will be given by the angle $\chi = \tan^{-1}(v/u)$ measured from the polar axis.[6] Since equations (20) and (21) hold only for steady circulation, we see at once that under this condition the instantaneous stream lines, $\psi=$constant obtained by plotting the directions χ or $\tan^{-1}(v/u)$ are the same whether the axes are fixed in space or rotate with the earth. We see also that the stream lines $\psi'=$ constant, which will be obtained by plotting the directions $\tan^{-1}[(v+\omega\varpi)/u]$ would not change with time, and would thus continue to remain stream lines with reference to axes fixed in space for all time to come. These would therefore, as already indicated, represent the paths of the particles. In synoptic representation, it is the function ψ which we have to consider and not the function ψ'. There is nothing instantaneous in ψ'; it is true for all time.

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[6] One axis, *i.e.*, polar axis, is sufficient for the determination of the direction on a plane surface.

(3) The statement of Dr. Savur that " in steady air motion the isobars coincide with stream lines as drawn with respect to axes instantaneously at rest " is not a *correct* representation of what I said in my papers. I have used everywhere the expression " synoptic isobars " or " instantaneous configuration of isobars " and not simply " isobars " as Dr. Savur does [see p. 716 of (2)]. It is because Dr. Savur has not grasped the precise meaning of synoptic observations (or observations taken instantaneously and at the same *instant*) under *steady* circulation that he is meeting with all these difficulties. It is not correct to say that no proof has been given of the proposition. Definite proof has been given in the first paragraph of page 717 of paper (2).

Our barometers record the dynamic pressure, that is to say, they record the pressure p as given by (17). When the circulation is steady, P is given by integrating equations (20) and (21). If ψ is the stream function, then we can write

$$v = -\frac{\partial\psi}{\partial x} \qquad u = \frac{\partial\psi}{\partial y} \tag{25}$$

Consequently on integration we get

$$P = -2\,\omega\cos\theta.\psi + \text{constant.}$$

and by (17),

$$\frac{p}{\rho} = -2\,\omega\cos\theta.\,\psi - \Omega + \tfrac{1}{2}\,\omega^2\,\varpi^2 + \text{constant,}$$

or

$$\frac{p}{\rho} = -2\,\omega\cos\theta.\,\psi - gz + \tfrac{1}{2}\,\omega^2\,\varpi^2 + \text{constant.} \tag{26}$$

We see that under steady circulation p is independent of t, and as p is a scalar function, the instantaneous values of p are the same whether the axes rotate with the earth or are fixed in space. The configuration of *synoptic* isobars under steady circulation is therefore the same whether the axes are instantaneously fixed in space or rotate with the earth.

I have explained above that when the circulation is steady the instantaneous values of the scalar function ψ are the same whether the axes are fixed in space or rotate with the earth. If we limit our discussion to a small area over a level surface then Ω is constant and so also $\varpi^2 \omega^2$ over the surface. Consequently equation (26) gives that when p = constant, ψ is also = constant. In other words, the isobars coincide with stream lines. It is thus obvious that the *synoptic* isobars and *instantaneous* configuration of stream lines coincide with one another, whether the axes are instantaneously fixed in space or rotate with the earth. It will thus be clear that there is no conflict whatsoever with Col. Gold's results or Lord Rayleigh's results referred to by Dr. Savur. Lord Rayleigh in his paper starts with the remark that "an instantaneous derivation of the formula for the gradient wind has been given by Gold," writes his equations with reference to axes instantaneously fixed in space and in the subsequent discussion never changes them to rotating axes.[7] Strictly speaking therefore his results are true with reference to axes instantaneously fixed in space. The mere fact that he expressed his equations in terms of the relative velocity or the relative stream function does not change his axes to rotating axes. When, however, stress is laid on the word "instantaneous" with which Lord Rayleigh begins and the fact that in the latter part of his discussion he considers a steady motion, it is immaterial whether the axes are considered to be instantaneously fixed in space or to rotate with the earth.

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[7] Lord Rayleigh's equation (6) from which the gradient equation is deduced refers to the instantaneous position of the axis of x, which at the moment coincides with the line "perpendicular to the direction of relative motion at any point," This is clear because this equation is the same as his equation (3), which explicitly refers to the instantaneous position of the x-axis.

In regard to Dr. Savur's remark relating to Stokes' solution used by me on p. 715 of (2), I would point out that on page 713 of (2), I take the most general expression for the stream function and use Stokes' solution merely to find out which terms are most important in the neighbourhood of the rectangular corner over Bengal. I have given brief explanation on pp. 729-32 of paper (2) as to how the solutions have been used in tracing the stream lines. I have indicated in the first part of this note how the constants are determined and the form of the stream function inside and outside the corner. It is of course not possible to give detailed numerical values of these constants in this brief reply.

When we take viscosity of air into consideration, the equations[8] (20) and (21) will become

$$\left.\begin{aligned} -2\omega \cos\theta\, v &= \frac{\partial P}{\partial x} + k\frac{\partial^2 u}{\partial z^2}, \\ 2\omega \cos\theta \cdot u &= -\frac{\partial P}{\partial y} + k\frac{\partial^2 v}{\partial z^2}, \end{aligned}\right\} \qquad (27)$$

The terms $\frac{\partial^2 u}{\partial z^2}, \frac{\partial^2 v}{\partial z^2}$ involve vertical variation of wind. In free air when there is a steady horizontal circulation, we can neglect the vertical variation of wind. We see from the form of the dynamical equations that on this assumption, the viscosity terms are negligible. It was on this ground, which has been clearly explained in my papers, that the equations of motion of a perfect fluid were used. Within the limit of approximation, as explained therein, the method adopted is fully justified. The agreement between the observed and theoretical stream lines gives a complete confirmation of the correctness of the procedure.

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[8] Jeffreys, *loc. cit.*

34

A Note on the Shape of the Electro-capillary Curve of Mercury in Capillary Inactive Electrolytes.

By

R. M. Joshi, M.SC.

(Received for publication, 9th September, 1932.)

F. O. Koenig[1] has recently stated that when alkali salts are used as foreign electrolytes, amalgam formation most probably plays no part in the electro-capillary curve. In this connection, it was thought to be of interest to publish the following observation.

The electro-capillary curve for mercury in 1N-NaNO was obtained by using a form of Lippmann capillary-electrometer in which mercury was below and the electrolyte above. While the curve at first sight looked like a parabola, on a further investigation it was found that the right-hand side was displaced inward and that it extended a little below the axis of applied potential. This showed that the surface tension of the mercury had fallen slightly below the initial value, *i.e.*, when the applied potential was zero. Also, while cleaning the apparatus, it was noticed that a small quantity of mercury at the meniscus adhered to the glass-capillary and yielded a pink tinge with a drop of phenolphthalein. This

[1] Z. f. Phy. Chem., *154*, 421 (1931).

indicates that a slight quantity of amalgam had formed at the meniscus of the mercury.

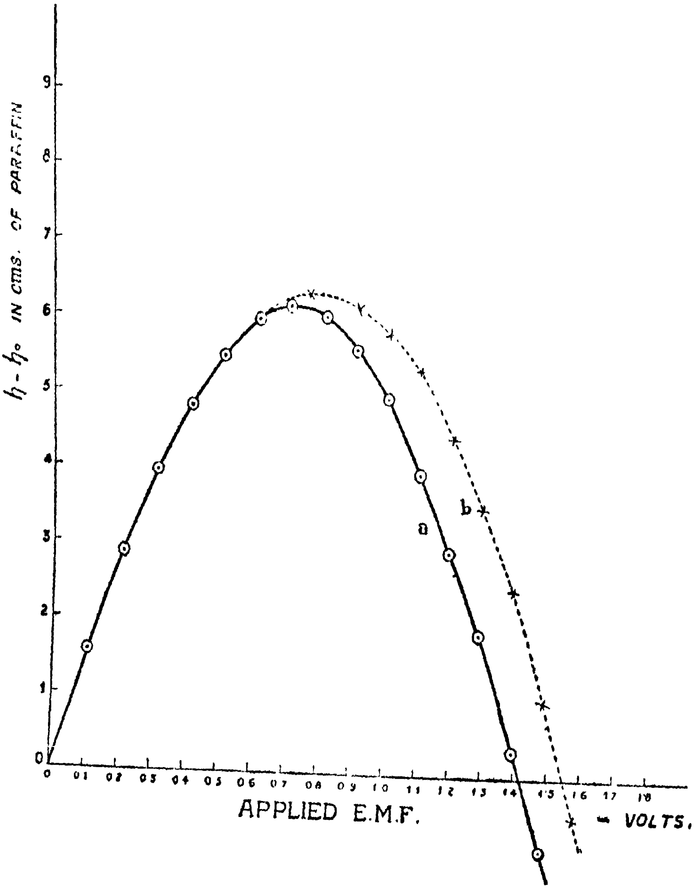

FIG. 1.

The curve obtained in 1N-NaNO$_3$ was quite similar to that obtained by Krüger and Krumreich[2] in 1N-KNO$_3$ with the usual Lippmann arrangement. These authors have shown in the same paper that a necessary consequence of the Lippmann-Helmholtz theory is that the curve shall be a parabola. Together with later workers (*cf.* Freundlich, Colloid and Capillary Chemistry, trans. Hatfield (1926), p. 290), they assumed that in capillary inactive electrolytes, conditions are much as required by the Lippmann-Helmholtz theory. The double layer behaves like a condenser; at the maximum of the electro-capillary curve we have zero charge, the mercury has a positive charge on the ascending limb of the curve and a negative one on the descending limb.

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[2] Z. f. Electro-Chem., *19*, 617 (1913).

When it is remembered that both KNO_3, and $NaNO_3$ are capillary inactive electrolytes, it is surprising why they should not yield an exact parabola, but a curve of the type described above.

While the theories offered by Nernst,[3] Gouy[4] and Frumkin[5] take into account the adsorption of ions and neutral molecules at the interface, they do not consider electrolysis, which according to the general principles of electro-chemistry must start as soon as the contact potential is overcome, and must, therefore, manifest itself on the descending part of the curve.

The result of electrolysis must be the formation of an amalgam which was noticed repeatedly in these experiments. Since sodium and potassium both reduce the surface tension of mercury the descending branch should be displaced inwards as is observed in the author's curves in $NaNO_3$ (Fig. 1) and Krüger and Krumreiches' in KNO_3.

The curve *a* in Fig. 1 is plotted from the directly observed values of $(h\text{-}h_0)$ while the curve *b* is plotted by an extrapolation of the observed values of $(h\text{-}h_0)$ lying only on the ascending part of *a*. The so-called theoretical curve given by Krüger and Krumreich was calculated by them by using the method of least sqaures and taking into account all the observed values of $(h\text{-}h_0)$ and thus it was only a smoothened form of the observed curve.

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[3] Z. f. Elektrochem., 4, 29 (1897).

[4] Amr. Chim. Phys., 8 294 (1908).

[5] Z. f. Phys., 35, 792 (1926).

The equation they derived from the Lippmann-Helmholtz theory was parabolic and the same equation has been used in calculating the curve *b* of Fig. 1 in this paper.

Again it will be seen from Fig. 1 that the displacement of the observed curve does not begin exactly at the maximum as it should if electrolysis was the only additional factor to be considered. It begins earlier and this is to be referred to the slight change the capacity of the condenser undergoes owing to the change of the adsorptive power of the mercury surface by the applied potential.

Thus it will be seen that the original Lippmann-Helmholtz theory does not furnish a complete explanation of the behaviour of capillary-inactive electrolytes like KNO_3 and $NaNO_3$. The effect of electrolysis which begins as soon as the contact potential is overcome must be considered. The resulting amalgamation shifts inward the descending limb of the electro-capillary curve.

The author takes this opportunity to thank Prof. G. R. Paranjpe of this Institute for providing facilities for work in his Laboratory and to Dr. T. S. Wheeler, Principal of this Institute, for the interest he showed during the progress of the work.

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35

A Bibliography of the Raman Effect. 1930-32

By

S. C. SIRKAR.

Plan of the Bibliography.

The plan adopted in the classification of the various papers under different subject headings is the same as the one given in the earlier bibliography (Ind. Jour. Phys., **5**, *257*, 1931). The bibliography includes papers published from the beginning of July, 1930 to the end of August, 1932.

There is an author index ; against each author are given the letters of the alphabet indicating the sections in which his name appears.

An index of all the substances studied is also given. The inorganic substances are arranged alphabetically and the organic ones are arranged according to the plan adopted in the International Critical Tables.

It is hoped to publish a critical compilation of the Raman frequencies of all the substances investigated so far in a separate article.

A

Special Monographs.

1.	**Bhagavantam, S.**	The Raman Effect. Its significance for physics and chemistry. Ind. J. Phys., **5**, *237* (1930): Relation to earlier work. Nature of the effect. Its significance to spectroscopy. Raman effect and the structure of molecules. Raman effect and crystal physics. Raman effect and physical chemistry. Raman effect and the nature of valence. Raman effect and organic chemistry.
2.	**Kohlrausch, K. W. F.**	Report on the Smekal Raman Effect. Physikal. *Z.* **32**, *385* (1931): Historical introduction. Experimental survey. Theoretical survey. The structure of the undisplaced lines. The appearance of rotation frequencies. The intensity of scattered radiation. Dependence of the displacement $\Delta\nu$ on intermolecular forces. Raman effect and problems of molecular structure.
3.	**Osborne, D.**	Researches on light scattered by a crystal of calcite. University Press, Paris, 1932.
4.	**Raman, C. V.**	The molecular scattering of light. Nobel lecture. Ind. J. Phys., **6**, *263* (1931): The colour of the sea. The theory of fluctuations. The anisotropy of molecules. A new phenomenon. The optical analogue of the Compton effect. Its spectroscopic characters. Interpretation of the effect. The significance of the effect. Some concluding remarks.
5.		Light scattering and chemistry. Malaviya Commemoration Volume, *747* (1932): Nature of the effect. Significance of the effect. The spinning photon and the rotating molecule. The vibration of molecules. Relationship to infra red absorption. Mechanics of molecular oscillations. Significance of molecular models. The chemistry of carbon compounds.

B

Journal Articles.

1. ANDREWS, D. H.	Raman spectra.	Indust. Eng. Chem., 2 *1232* (1931).
2. DADIEU, A.	The Raman effect and its application to organic chemistry.	Z. f. Angewandte Chem **43**, *800* (1930).
3. DADIEU, A. AND KOHLRAUSCH, K. W. F.	Raman effect and Chemical problems.	J.O.S.A., **21**, *286* (1931)
4. ELSEN, G.	On Raman effect.	Chem. Weekbald, **29**, (1932).
5. HULTHEN, E.	Raman effect.	Kosmos, **7**, *111* (1929).
6. KOHLRAUSCH, K. W. F.	Raman effect and Chemistry.	Scientia, **51**, *335* (1932)
7. NIELSEN, J. R.	Recent discoveries concerning the interaction of light and matter.	School Sc. and Mat **29**, *394* (1929).
8. ,,	The Raman effect.	School Sc. and Mat **29**, *581* (1929).
9. SMEKAL, A.	The Raman effect and its significance for the spectroscopy of the molecular structure.	Z. f. Electro-chem., *618* (1930).
10. VELLUZ, L.	A new method of determining molecular structure; the Raman spectrum.	J. Pharm. Chim., *385* (1931).
11. WEILER, J.	Raman effect and molecular anisotropy.	Physikal. Z., **33**, (1932).
12. WENZEL, A.	The Raman effect	Z. f. Unterr., **43**, (1930).

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1. **BHAGAVANTAM, S.** The Raman Effect. Its significance for physics and chemistry. Ind. J. Phys., **5**, *237* (1930):
Relation to earlier work. Nature of the effect. Its significance to spectroscopy. Raman effect and the structure of molecules. Raman effect and crystal physics. Raman effect and physical chemistry. Raman effect and the nature of valence. Raman effect and organic chemistry.

2. **KOHLRAUSCH, K. W. F.** Report on the Smekal Raman Effect. Physikal. *Z.* **32**, *385* (1931):
Historical introduction. Experimental survey. Theoretical survey. The structure of the undisplaced lines. The appearance of rotation frequencies. The intensity of scattered radiation. Dependence of the displacement $\Delta\nu$ on intermolecular forces. Raman effect and problems of molecular structure.

3. **OSBORNE, D.** Researches on light scattered by a crystal of calcite. University Press, Paris, 1932.

4. **RAMAN, C. V.** The molecular scattering of light. Nobel lecture. Ind. J. Phys., **6**, *263* (1931):
The colour of the sea. The theory of fluctuations. The anisotropy of molecules. A new phenomenon. The optical analogue of the Compton effect. Its spectroscopic characters. Interpretation of the effect. The significance of the effect. Some concluding remarks.

5. Light scattering and chemistry. Malaviya Commemoration Volume, *747* (1932):
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3. DADIEU, A. AND KOHLRAUSCH, K. W. F.	Raman effect and Chemical problems.	J.O.S.A., **21**, *286* (1931).
4. ELSEN, G.	On Raman effect.	Chem. Weekbald, **29**, *1* (1932).
5. HULTHEN, E.	Raman effect.	Kosmos, **7**, *111* (1929).
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9. SMEKAL, A.	The Raman effect and its significance for the spectroscopy of the molecular structure.	Z. f. Electro-chem., **36**, *618* (1930).
10. VELLUZ, L.	A new method of determining molecular structure; the Raman spectrum.	J. Pharm. Chim., **14**, *385* (1931).
11. WEILER, J.	Raman effect and molecular anisotropy.	Physikal. Z., **33**, *489* (1932).
12. WENZEL, A.	The Raman effect	Z. f. Unterr., **43**, *273* (1930).

C

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1. Kohlrausch, K. W. F. Der Smekal Raman Effect. Julius Springer, Berlin, 1931.

D

Experimental Technique.

1. Almasy, F.	An apparatus of great intensity for photographing fluorescence and Raman spectra.	Physikal. Z., **33**, *221* (1932).
2. Bär, R.	On light-filters useful in experiments on Raman effect.	Helv. Phys., **5**, *174* (1932).
3. Barker, E. F.	Rotational fine structure in Raman spectra.	Phys. Rev., **37**, *330* (1931).
4. Bourguel, M.	Spectrograph for the study of Raman effect in the visible region of the spectrum.	Revue D'Optique, **10**, *474* (1931).
5. Buttolph, L. J.	Raman effect apparatus.	Rev. Sc. Inst., **1**, *650* (1930).
6. Grassmann, P.	On the methods in the Raman effect.	Z. f. Phys., **72**, *240* (1931).
7. Hulubei, H. and Cauchois, Y.	Simple and luminous arrangement for the study of Raman effect.	Compt. Rend., **192**, *935* (1931).
8.	Monochromatic excitation of Raman effect in the ultra violet.	Compt. Rend., **192**, *1640* (1931).
9. Krishnamurti, P.	Raman effect with cadmium arc excitation.	Ind. J. Phys., **5**, *587* (1930).
10. Nielsen, J. R.	The filling up of a spectrograph with light considered as a geometrical problem.	Jour. Opt. Soc. Am., **20**, *701* (1930).
11. Pal, N. N. and Sen Gupta, P. N.	The origin of continuous spectra in Raman scattering.	Ind. J. Phys., **5**, *609* (1930).
12. Todesco, G.	Microphotometric registration with photoelectric cell and thermionic amplifier.	Il Nuovo Cimento, **9**, *138* (1932).
13. Venkatesachar, B. and Sibaiya, L.	Study of Raman effect in certain substances with a new apparatus.	Ind. J. Phys., **5**, *747* (1930).
14. Wood, R. W.	Improved technique for the Raman effect.	Phys. Rev., **36**, *1421* (1930).
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16.	Raman effect in benzene substitution products by improved technique.	Phys. Rev., **38**, *2168* (1931).
17. Ziemecki, S.	Apparatus for investigating the Raman effect in organic compounds.	Bull. Inter. Acad. Polo., *309* (1930).

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Character of the Lines; Continuous Spectrum.

1.	Banerjee, K.	Relation of the liquid to the crystalline state.	Nature, **127**, *92* (1931).
2.	Bär, R.	On the experiments for the demonstration of continuous Raman effect in liquids.	Helv. Phys., **4**, *369* (1931).
3.	Biquard, P. and Lucas, R.	New optical properties of solids and liquids produced by the action of ultrasonic waves.	Compt. Rend., **195**, *121* (1932).
4.	Bolla, G.	Structure of the Raman band of water.	Nature, **128**, *546* (1931).
5.	Cabannes, J.	On the fine structure of spectral rays scattered by molecules.	Compt. Rend., **191**, *1123* (1930).
6.	Debye, P. and Sears, F. W.	On the scattering of light by supersonic waves.	Proc. Nat. Acad. Sc., **18**, *409* (1932).
7.	Gross, E.	On the change of wavelength through elastic heat waves at light scattering in liquids.	Naturwiss., **18**, *718* (1930).
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9.	,,	The splitting of spectral lines at scattering of light by liquids.	Nature, **126**, *400* (1930).
10.	,,	Splitting of the frequency of light scattered by liquids and optical anisotropy of molecules.	Nature, **126**, *603* (1930).
11.	,,	On the change of wavelength at light scattering in crystals.	Z. f. Phys., **63** *685* (1930).
12.	High, M. E. and Pool, M. L.	Removal of continuous background from Raman spectrum of carbon tetrachloride.	Phys. Rev., **38**, *374* (1931).
13.	Howlett, L. E.	Raman spectra of benzene and toluene.	Nature, **128**, *796* (1931)
14.	Kastler, A.	On the structure of Raman bands of liquids.	Compt. Rend., **192**, *1032* (1931).
15.	Langseth, A.	Fine structure of Raman lines in liquids.	Nature, **128**, *225* (1931)

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16. Langseth, A.	Fine structure of Raman bands.	Z. f. Phys., **72**, *350* (1931).
17. Mesnage, P.L.	Essay on the employment of large dispersion in the study of Raman effect.	Jour. de Phys., **2**, *403* (1931).
18. Meyer, E. H. L. and Ramm, W.	The structure of Rayleigh radiation.	Physikal. Z., **33**, *270* (1932).
19. Ney, M. J.	On the spreading of the spectral line scattered in Raman effect without change of frequency.	Compt. Rend., Soc. Polo. Phys., **5**, *389* (1931).
20. Pal, N. N. and Sen Gupta, W. P. N.	The origin of continuous spectra in the Raman scattering.	Ind. J. Phys., **5**, *609* (1930).
21. Placzek, G. and Van Wijk, R.	On the continuous Raman spectrum and its behaviour at the critical point.	Z. f. Phys., **70**, *287* (1931).
22. Rafalowski, S.	Structure of the Raman band of water	Nature, **128**, *546* (1931).
23. ,,	The fine structure of spectral lines of light scattered by liquids.	Nature, **128**, *495* (1931).
24.	On the fine structure of the rays of light scattered by liquids.	Acta Phys. Polo., **1**, *117* (1932).
25. Raman, C. V.	Doppler effect in light scattering.	Nature, **128**, *636* (1931).
26. Rousset, A.	Cabannes—Daure effect and molecular field.	Compt. Rend., **194**, *2299* (1932).
27. Thatte, V. N. and Shahane, S. M.	The Raman spectra of glycol and some organic chlorine compounds.	Ind. J. Phys., **6**, *155* (1931).
28. Vacher, M.	On the modification of fine structure of spectral rays by molecular scattering. Studies on the function of angle of scattering.	Compt. Rend., **191**, *1121* (1930).

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1. Bhagavantam, S.	A study of the Raman effect in amorphous solids.	Ind. J. Phys., **6**, *1* (1931).
2. ,,	Raman effect in gases. I. Some experimental results.	Ind. J. Phys., **6**, *319* (1931).
3.	Intensity of Raman scattering in gases.	Nature, **128**, *272* (1931).
4.	Evidence for a spinning photon, I. Intensity relations in the Raman spectrum of hydrogen.	Ind. J. Phys., **7**, *107* (1932).
5. Billroth, H.C., Kohlrausch, K. W. F. and Pongratz, A.	Quantitative estimation of isomerisation with the help of Raman effect.	Z. f. Phys. Chem. B., **17**, *233* (1932).
6. Carelli, A. and Went, J. J.	Intensity measurements in Raman spectra.	Z. f. Phys., **76**, *236* (1932).
7. Crigler, E. A.	Intensity of Raman lines in estimating the concentration of compounds present in benzene.	Phys. Rev., **38**, *1387* (1931).
8 Ellenberger, G.	Intensity measurements of Raman lines.	Ann. der Phys., **14**, *221* (1932).
9. Landsberg, G. and Mandelstam, S. L.	Molecular scattering of light in solid bodies.	Z. f. Phys., **73**, *502* (1931).
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11. Rekveld, J.	On the frequency dependence of Raman radiation.	Z. f. Phys., **68**, *543* (1931).
12. Roy Choudhuri, D. P.	The angle distribution of the intensity of Raman lines.	Z. f. Phys., **72**, *242* (1931).
13. Segre, E.	Intensity of the rotational lines in the Raman effect in diatomic molecules.	Il Nuovo Cimento, **7**, *380* (1930).
14. Sirkar, S. C.	Further investigations on the intensities of lines in Raman spectra.	Ind. J. Phys., **5**, *593* (1930).

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15.	SIRKAR, S. C.	On the relative intensities of different Raman lines due to different exciting frequencies.	Ind. J. Phys., (1930).	**5**, *663*
16.		The influence of exciting frequency on the intensities of lines in Raman spectra.	Ind. J. Phys., (1931).	**6**, *133*
17.		On the relative intensities of Stokes and anti-Stokes lines in the Raman spectrum.	Ind. J. Phys., (1931).	**6**, *295*
18.	WEILER, J.	Intensity distribution in the Rayleigh lines in organic liquids.	Z. f. Phys., (1931).	**68**, *782*
19.		Remarks on the intensity and polarisation of scattered lines due to ring formed hydrocarbons.	Z. f. Phys., (1931).	**72**, *206*
20.	WERTH, SISTER M.	Relative efficiency of the Hg arc lines in exciting the Raman spectrum of benzol.	Phys. Rev., (1930).	**36**, *1096*
21.		Relative efficiency of some of the mercury arc lines in exciting Raman spectrum of benzol.	Phys. Rev., (1932).	**39**, *299*

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2. BÄR, R.	On the polarisation of the Raman lines in carbon tetrachloride, benzene and sulphur trioxide.	Helv. Phys. Acta, **4**, *130* (1931).
3. ,,	On an anomaly in the polarisation of Raman rediation.	Naturwiss., **19**, *463* (1931).
4. ,,	Atoms and molecules as Fitzgerald oscillators.	Nature, **129**, *505* (1932)
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6. ,,	Polarisation of Raman scattering by hydrogen.	Nature, **128**, *70* (1931).
7.	Raman effect in gases, III. Comparison of theory and experiment.	Ind. J. Phys., **6**, *557* (1931).
8.	Polarisation of Raman lines in liquids.	Ind. J. Phys., **7**, *79* (1932).
9.	The spinning photon and its scattering by molecules.	Nature, **129**, *167* (1932).
10.	Evidence for a spinning photon, I. Intensity relations in the Raman spectrum of hydrogen.	Ind. J. Phys., **7**, *107* (1932).
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12. CABANNES, J.	Rules of polarisation of Raman lines in crystals.	Compt. Rend., **194**, *2134* (1932).
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15. COTTON, A.	Remarks on the preceding note of A. Kastler.	Compt. Rend., **193**, *1078* (1931).
16. HANLE, W.	On an anomaly in the polarisation of Raman radiation.	Naturwiss., **19**, *375* 1931).
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R—(*Contd.*)

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8

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T

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T—(*Contd.*)

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T—(*Contd.*)

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T—(*Contd.*)

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T—(*Contd.*)

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V

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W

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X

Theory.

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X—(*Contd.*)

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AUTHOR INDEX

Aderhold H. ... GLRT
Allard J. ... T
Almasy F. ... D
Amaldi E. ... H
Andrews D. H. ... BR
Angus W. R. ... I
Arakatsu B. ... G

Bailey C. R. ... IR
Ball G. N. ... T
Banerjee K. ... E
Bär R. ... DEGQ
Barker E. F. ... DHI
Barnes R. B. ... I
Bartels H. ... X
Bearden J. A. ... W
Bell R. M. ... N
Bhagavantam S. ... AFGHIKLMQRX
Bhargava S. ... W
Bhargava Y. ... G
Billroth H. C. ... FR
Biquard P. ... E
Biswas S. C. ... MR
Bolla G. ... EP
Bonino G. B. ... HT
Bose D. M. ... S
Bourguel M. ... DPRST
Bowers H. E. ... KRST
Bradley C. A. ... RT
Braune H. ... N
Brüll L. ... T
Brunetti R. ... NP
Buttolph L. J. ... D

Cabannes J. ... EGLRX
Callihan D. ... P
Canals E. ... LPT
Carelli A. ... F
Cassie A. B. D. ... IR
Cauchois Y. ... D
Cauquil G. ... PT
Cella P. ... HT
Childs W. H. J. ... H
Cleeton C. E. ... R
Collins G. ... T
Cork J. M. ... W
Cotton A. ... G
Cremer E. ... M
Crigler E. A. ... FP

Dadieu A. ... BRT
Damaschun I. ... ST
Das S. K. ... T
Datta S. ... S
Daure P. ... HMT
Debye P. ... E
Dennison D. M. ... I
Deslanders H. ... R
Dufford R. T. ... RS
Dupont G. ... T

Ellenberger G. ... F
Ellis J. W. ... IN
Elsen G. ... BR
Embirikos N. ... N
Engelbrecht G. ... N
Euler H. V. ... PT

Ffolliot C. F. ... T
Franklin D. ... P
Farnsworth Marie ... T
Fredrickson W. R. ... N

Ganesan A. S. ... ST
Ganguli A. ... X
Ghosh J. C. ... T
Gibbs R. C. ... I
Gingrich N. S. ... W
Godchot M. ... PT
Grassmann P. ... DN
Grédy B. ... T
Gross E. ... E

Hanle W. ... G
Harkins W. D. ... KRST
Hatley C. C. ... P
Hedfeld K. ... H
Heisenberg W. ... X
Hellström H. ... PT
High M. E. ... EIT
Hollaender A. ... N
Holmes F. T. ... H
Houston W. V. ... HX
Howlett L. E. ... ERS
Hulthen E. ... B
Hulubei H. ... DP

Imanishi S. ... T

Jele F. ... T
Johnson J. R. ... I
Johnston H. L. ... M
Joos G. ... T

Kar D. C. ... T
Kastler A. ... EGHMORTU
Kettering C. F. ... R
Kinsey E. L. ... N
Kohlrausch K. W. F. ... ABCFRT
Krishnamurti P. ... DILNPSU
Krönenberger A. ... K
Kutzner W. ... T

Laird E. R. ... NP
Landsberg G. ... F
Langseth A. ... EHI
Lechner F. ... R
Leontowitsch M. ... X
Lespieau R. ... PT
Levy J. ... T
Lewis C. M. ... H
Lindsay G. A. ... W
Loomis F. W. ... V
Lu S. S. ... T
Lucas R. ... E

Mahanti P. C. ... R
Mandelstam S. L. ... FX
Manneback C. ... X
Martin W. H. ... PT
Matossi F. ... GLRT
Mayer M. G. ... X
McLennan J. C. ... HM
Mecke R. ... HR
Menzies A. C. ... IMR
Mesnage P. L. ... E
Meyer E. H. L. ... EO
Mlodzianowska H. ... RT
Morris C. S. ... RT
Mukherjee J. B. ... W

Nevgi G. B. ... T
Ney M. J. ... EQ
Nielsen J. R. ... BDIN
Nisi H. ... LTU
Nordstrom C. H. ... X
Nutting F. L. ... W

Ollano Z. ... NPT
Ornstein L. S. ... FX
Osborne D. ... AGLX
Ota K. ... G

Pal N. N. ... DER
Paramasivan S. ... R
Parthasarathy S. ... GNOQ
Pauling L. ... L
Pestemer M. ... T
Piaux L. ... S
Pienkowski S. ... G
Placzek G. ... EGHX
Plyler E. K. ... I
Polanyi M. ... M
Polara V. ... T
Pongratz A. ... FRT
Pool M. L. ... E
Pringle C. O. ... M

Radakovic M. ... R
Rafalowski S. ... ENP
Raman C. V. ... AEG
Ramaswamy C. ... G
Ramm W. ... E
Rao I. R. ... NPQ
Rasetti F. ... HKL
Ray B. B. ... W
Redlich O. ... T
Rekveld J. ... FX
Ricca V. ... N
Rousset A. ... EGRX
Roy Choudhuri D. P. ... F

Saha M. N. ... G
Salant E. O. ... I
Sandow A. ... I
Schaefer C. ... GL
Scilowski C. ... R

Sears F. W. E
Segre E. FHPT
Sen Gupta P. N. DER
Shahane S. M. EIT
Shapiro C. V. I
Shutts I. W. R
Sibaiya L. DQ
Signer R. R
Silveira M. A. N
Sirkar S. C. F.I.
Sleator W. W. I
Smekal A. B
Smith H. D. HM
Specchia O. GNOQ
Sterling V. N
Stuart H. A. G
Sutherland G. B. B. M. T

Thatte V. N. EIST
Todesco G. D
Tomaschek R. L
Trumpy B. IPT
Tuuk J. H. Van Der W

Urey H. C. R

Vacher M. E
Van Wijk W. R. EG
Velluz L. B
Venkatesachar B. DQ
Venkateswaran S. GT
Villars D. S. P
Volkomann H. G

Wakeman R. L. PT
Walker M. K. M
Weiler J. BFGPR
Went J. J. F
Wenzel A. B
Werth Sister M. F
West W. T
Whiting R. E. PT
Wilhelm J. O. HM
Williams J. W. N
Winans J. G. V
Wolfke M. Q
Wood R. W. DP
Woodward L. A. N
Wright N. I

Yates R. C. RS

Ziemecki S. DQ

SUBSTANCE INDEX

Inorganic

A

Alum, L 13, 19; N 8.
,, (sol.), L 13.
Ammonia, E 15; H 1.
,, (liq.), R 13.
,, (sol.), H 11; N 19.
Ammonium acetate, L 11.
,, bromide, R 20.
,, carbonate, L 19.
,, chloride, H 8; R 20.
,, ,, (sol.), L 10.
,, fluoride, R 20.
,, molybdate, L 8; T 32.
,, oxalate, L 11.
,, perchlorate, L 8.
,, ,, (sol.), T 49.
,, phosphate, L 19.
,, sulphate, L. 13.
,, ,, (sol.), N 6.
,, thiocyanate, L 9.
Anhydrite, L 17, 18.
Antimony pentachloride, T 52.
Apatite, L 14.
Aragonite, L 3, 17, 18, 19; Q 8.
Arsenic trichloride, G 14.

B

Barite, L 13, 17, 18, 19; N 8.
Barium chlorate, L 8.
,, hydroxide, L 9.
,, nitrite (sol.), T 22.
,, thiocyanate, L 9.
Beryl, L 14.
Beryllium sulphate, L 13.
Beryllonite, L 14.
Boron trichloride, T 64.

C

Cadmium acetate, L 11.
,, ammonium chloride (sol.), T 26, 38.
,, iodide (sol.), N 3.
,, nitrate (sol.), N, 7.
,, sulphate, L 13; N 6.
Calcite, G 13, 34, 35; L 3, 16, 18, 19, 21; N 6; Q 8.
Calcium nitrate (sol.), N 7.
,, nitrite (sol.), T 22.
Carbon dioxide, H 3, 9, 10 ; I 11.
,, ,, (liq.), M 3.
Cerussite, L 19.
Chalk, L 17, 18.
Chlorine (liq.), T 20.
Copper ammonium chloride (sol.), T 26, 38.
,, ,, sulphate (sol.), T 26, 38.
,, sulphate, L 13; N 8; U 2.
,, ,, (sol.), L 13.
Cyanogen, H 6.

D

Danburite, L 14.
Diamond, L 1, 2.

F

Ferrous ammonium sulphate, L 13.
,, sulphate, L 7, 13 ; U 2.
,, ,, (sol.), L 13 ; U 2.
Fluorite, L 16, 18, 21 ; Q 8.

G

Glass, F 1; N 8.
Gypsum, G 34, 35; L 13, 19; N 6, 8.

H

Helium (liq.), H 13.
Hexamine cobaltous chloride (sol.), S 1.
,, cobaltic chloride (sol.), S 1.
Hydrazine, T 37, 54.
,, hydrate, T 37, 54.
Hydrochloric acid, N 27; O 1.
Hydrochlorostannic acid, T 52.
Hydrofluoric acid, N 27.
Hydrogen, F 3, 4; G 6; H 3, 6.
Hydrogen bromide, I 24, 25.
,, ,, (liq.), I 25.
,, chloride, I 25.
,, ,, (liq.), I 25.
,, cyanide (liq.), R 4; T 15, 16, 17.
,, iodide, I 24, 25.
,, peroxide, T 65.
,, sulphide, H 3 ; M 1.
,, ,, (liq.), M 1; R 13.

I

Ice, L 17, 18.
Iodic acid, L 8.
,, ,, (sol.), N 27.

L

Lead acetate, L 11.
,, ,, (sol.), L 11.
Lithium potassium sulphate, L 19.
,, sulphate, L 13.
,, ,, (sol.), N 6.

M

Magnesite, L 19.
Magnesium chlorate (sol.), N 21.
,, chloride (sol.), N 21.
,, nitrate (sol.), N 21.
,, sulphate, L 13; N 6, 8; U 2.
Manganese sulphate, L 13 ; U 2.
,, ,, (sol.), L 13 ; N 6.
Mercuric ammonium chloride, L 10.
,, ,, ,, (sol.), L 10.
,, bromide, L 10.
,, ,, (sol.), N 2.
,, chloride, L 10.
,, ,, (sol.), L 10; N 2, 24, 27.
Mercuric cyanide, L 9.
,, ,, (sol.), N 3, 24, 27.
,, iodide (sol.), N 3.
Metachloroantimonic acid, T 52.
Monochlorohexamine cobaltous chloride (sol.), S 1.
Monochloro sulphuric acid, R 25.
Nickel ammonium chloride (sol.), T 26.
,, sulphate, L 7, 13.
,, ,, (sol.), L 13.

N

Nitric acid, E 2; L 19; N 6, 13, 25, 27; T 21, 22.
,, oxide, H 14, 15.
Nitrogen, H 3; I 11; Q 2.
,, peroxide (solid), M 9.
Nitrous oxide, H 3; I 4, 11, 21.
,, ,, (liq.), M 8.

O

Oxygen, H 3, 17; I 11; Q 2.

P

Perchloric acid (sol.), T 49.
Phenacite, L 14.
Phosphoric acid, T 32.
Phosphorus oxychloride, E 16; T 48, 64.
,, tribromide, T 60.
,, trichloride, G 14; T 48, 60, 64.
Potassium bromate, L 8.
,, cadmium chloride (sol.), N 3.
,, ,, cyanide (sol.), T 26.
,, ,, iodide (sol.), N 3.
,, carbonate (sol.), N 6.
,, chlorate, L 8.
,, chromium cyanide (sol.), T 26.
,, cobalt ,, (sol.), T 26.
,, copper ,, (sol.), N 3; T 26.
,, cyanide (sol.), N 24, 27; T 15.
,, ferrocyanide, L 9.
,, ,, (sol.), T 26.
,, hydrogen sulphate (sol.), N 27.
,, hydroxide (sol.), N 15, 26, 27; T 49.

Potassium iodate, L 8.
,, mercuric bromide (sol.), N 3.
,, ,, chloride (sol.), N 3.
,, ,, cyanide (sol.), N 3.
,, ,, iodide (sol.), N 3.
,, nitrite (sol.), T 22.
,, perchlorate (sol.), T 49.
,, periodate, L 8.
,, silver cyanide (sol.), L 9; N 3.
,, ,, iodide (sol.), N 3.
,, sulphate, L 13; N 6.
,, thiocyanate, L 9.
,, zinc cyanide (sol.), T 26.

Q

Quartz, F 9; L 17, 18; Q 4.

R

Rock salt, L 16; Q 8.
Rubidium sulphate, L 13.

S

Silico chloroform, R 37; T 12.
Silicon tetrabromide, T 60.
,, tetrachloride, G 8, 11; T 59, 60.
Silver ammonium chloride (sol.), T 26.
Sodium acetate (sol.), T 31.
arsenate (sol.), T 32.
arsenite (sol.), T 32.
benzoate (sol.), T 31.
bromate, L 8, 19.
carbonate (sol.), N 6.
chlorate, L 8, 19.
citraconate (sol.), T 58.
cyanide, L 9.
formate (sol.), T 31.
fumarate (sol.), T 58.
hydrogen phosphite (sol.), T 32.
,, sulphide (sol.), T 32.
,, sulphite (sol.), T 32
hydroxide, L 9.
,, (sol.), N 15, 26, 27; T 49.
hypophosphite (sol.), T 32.
maleate (sol.), T 58.
malonate (sol.), T 31.
Sodium mesaconate (sol.), T 58.
metaborate (sol.), T 32.
metaphosphate (sol.), T 32.
metavanadate (sol.), T 32.
monochloroacetate (sol.), T 31.
nitrate, G 34, 35; L 6, 19.
,, (sol.), N 23, 27.
nitrite (sol.), T 22, 32.
orthovanadate (sol.), T 32.
perchlorate, L 8.
,, (sol.), T 49.
persulphate (sol.), T 32.
phosphite (sol.), T 32.
sulphate, L 13.
trichloroacetate (sol.), T 31.
tungstate, L 8.
,, (sol.), T 32.
Strontium sulphate, L 13.
Sulphur, L 7, 10; R 25.
,, chloride, R 25; T 48, 64.
,, dioxide, H 3; R 4.
,, ,, (liq.), R 13, 25; T 48.
Sulphuric acid, E 2; N 1, 20, 22, 25, 27.
Sulphurous acid, T 48.
Sulphur trioxide, G 2.
Sulphuryl chloride, E 16; R 25; T 48.

T

Thionyl chloride, R 25; T 48, 64.
Tin tetrabromide (melt.), T 59.
Tin tetrachloride, E 16; G 8, 11; T 59.
Titanium tetrachloride, G 8, 11; T 59.
Topaz, L 14.
Tourmaline, L 14.

W

Water, D 8; E 4, 15, 22; G 32, 36; N 4, 17; P 1, 7, 8, 13; Q 6, 7; T 31.
Water (vap.), H 6; M 7.

Z

Zinc acetate, L 11.
,, ammonium chloride (sol.), T 26.
,, ,, sulphate (sol.), T 26, 38.
,, sulphate, L 13; U 2.
,, ,, (sol.), N 6.
Zircon, L 14.

Organic

CBr_4	Carbon tetrabromide (sol.)	E 16; T 20.
CCl_2F_2	Dichlorodifluoro methane	T 12.
CCl_2O	Phosgene (liq.)	T 20.
CCl_4	Carbon tetrachloride	E 16, 17; F 6, 8, 14, 16, 17; G 2, 3, 8, 11, 16, 17, 18, 25; T 59.
COS	Carbonyl sulphide (liq.)	R 13.
CS_2	Carbon disulphide	E 17; G 8, 9, 23; I 2, 7, 14; R 4, 25; T 67.
	,, (mixt.)	T 67.
$CHBrCl_2$	Dichlorobromomethane	T 3.
$CHBr_3$	Bromoform	T 18.
$CHCl_2F$	Dichloro fluoromethane	T 12.
$CHCl_3$	Chloroform	G 16, 17, 18; R 11; T 18.
CH_2Br_2	Methylene bromide	T 18, 20.
CH_2Cl_2	Methylene chloride	F 8.
CH_2I_2	Methylene iodide	T 18.
CH_2O	Formaldehyde (sol.)	L 11.
CH_2O_2	Formic acid	O 3.
CH_3Br	Methyl bromide (liq.)	R 11; T 1.
CH_3Cl	Methyl chloride (liq.)	T 1, 66.
CH_3F	Methyl fluoride (liq.)	T 1.
CH_3I	Methyl iodide	R 11; T 1, 20
$CH_3Mg\ Br$	Methyl magnesium bromide	R 11.
CH_3MgI	Methyl magnesium iodide	R 11.
CH_3NO	Formamide	T 19.
CH_3NO_2	Methyl nitrite (liq.)	T 22.
CH_3NO_3	Methyl nitrate	S 6; T 22.
CH_4	Methane	R 5, 6.
CH_4N_2O	Urea	L 11.
	,, (sol.)	L 11.
$CH_4N_2O_2$	Methyl nitramine (sol.)	T 19.

CH_4O	Methyl alcohol	F 11; G 17; N 14; T 31, 67.
	,, (mixt.)	E 21; O 2.
CH_5ClN_2O	Urea hydrochloride (sol.)	N 13.
C_2Cl_4	Tetrachloro ethylene	T 46, 57.
C_2Cl_6	Hexachloro ethane	L 11.
C_2HCl_3O	Chloral	T 19, 57.
$C_2HCl_3O_2$	Trichloro acetic acid (sol.)	N 27; T 31
C_2HCl_5	Pentachloro ethane	T 50, 57
C_2H_2	Acetylene	H 3, 6; I 11; Q 8; T 53.
$C_2H_2Br_2$	1, 2-Acetylene dibromide	R 7; T 23.
	,, (cis.)	R 14.
	,, (trans.)	R 14.
$C_2H_2Br_4$	1, 1, 2, 2-Tetrabromo ethane	R 11.
$C_2H_2Cl_2$	1, 2-Acetylene dichloride (cis)	T 2, 50.
	,, ,, (trans.)	T 2, 50.
$C_2H_2Cl_2O$	Chloroacetyl chloride	T 19.
$C_2H_2Cl_2O_2$	Dichloro acetic acid	N 27; T 46, 56.
$C_2H_2Cl_4$	1, 1, 2, 2-Tetrachloro ethane	E 17; F 8; R 11; T 57.
$C_2H_2O_4$	Oxalic acid	L 11.
C_2H_3Br	Vinyl bromide (liq.)	T 10.
C_2H_3Cl	Vinyl chloride (liq.)	T 10, 50, 66.
C_2H_3ClO	Acetyl chloride	T 56.
$C_2H_3ClO_2$	Monochloroacetic acid (sol.)	T 31.
C_2H_3N	Acetonitrile	T 15.
C_2H_3N	Methyl isocyanide	T 15.
C_2H_4	Ethylene (liq.)	T 10.
$C_2H_4Br_2$	Ethylene bromide	R 11.
$C_2H_4Br_2$	Ethylidene bromide	R 11.
$C_2H_4Cl_2$	Ethylene chloride	R 11; T 50.
$C_2H_4Cl_2$	Ethylidene chloride	R 11; T 50.
$C_2H_4N_4$	Dicyan diamide (sol.)	T 19.
$C_2H_4O_2$	Acetic acid	F 8; I 19; N 14; T 31, 67.
	,, (mixt.)	P 9; T 67.
C_2H_5Br	Ethyl bromide	R 11.
C_2H_5Cl	Ethyl chloride (liq.)	R 11; T 20, 66.
C_2H_5I	Ethyl iodide	R 11; T 20.
$C_2H_5NO_2$	Ethyl nitrite (liq.)	T 22.
$C_2H_5NO_2$	Nitro ethane	T 22.
$C_2H_5NO_3$	Ethyl nitrate	T 22.

C_2H_6	Ethane	R 5.
C_2H_6O	Ethyl alcohol	D 8; G 17; I 27; T 48.
C_2H_6O	Methyl ether (liq.)	T 19.
$C_2H_6O_2$	Glycol	T 46, 57, 67.
$C_2H_6O_3S$	Dimethyl sulphite	R 25.
C_2H_6S	Dimethyl sulphide	R 25; T 63.
$C_2H_6S_2$	Methyl disulphide	T 63.
C_2H_7N	Dimethyl amine (liq.)	T 18.
$C_2H_8N_2$	Ethylene diamine	T 19.
$C_3H_3NO_2$	Cyanoacetic acid (sol.)	T 15.
C_3H_4	Allene (liq.)	S 3.
C_3H_4O	Acrolein	T 10.
$C_3H_4O_2$	Acrylic acid	T 10.
$C_3H_4O_4$	Malonic acid (sol.)	T 31.
C_3H_5Br	Allyl bromide	S 7; T 10.
C_3H_5Cl	Allyl chloride	T 10.
C_3H_5Cl	1—Chloropropylene	T 50.
C_3H_5Cl	2—Chloropropylene	T 50.
C_3H_5Cl	3—Chloropropylene	T 50.
$C_3H_5ClO_2$	Ethyl chloroformate	T 19.
C_3H_5N	Propionitrile	T 18.
C_3H_5N	Ethyl isocyanide	T 15.
C_3H_5NS	Ethyl thiocyanate	T 15.
C_3H_5NS	Ethyl iso-thiocyanate	T 15.
C_3H_6	Cyclopropane (liq.)	T 13.
C_3H_6	Propylene (liq.)	T 10.
$C_3H_6Br_2$	1,3—Dibromopropane	T 20.
$C_3H_6Cl_2$	1,1—Dichloropropane	T 50.
$C_3H_6Cl_2$	1,2—Dichloropropane	T 50.
$C_3H_6Cl_2$	1,3—Dichloropropane	T 50.
$C_3H_6Cl_2$	2,2—Dichloropropane	T 50.
C_3H_6O	Allyl alcohol	T 10.
C_3H_6O	Acetone	I 27; T 67.
	” (mixt.)	T 67.
$C_3H_6O_2$	Ethyl formate	T 31.
C_3H_7Br	*n*—Propylbromide	S 7.
C_3H_7Br	Isopropyl bromide	S 7; T 25.
C_3H_7Cl	*n*—Propyl chloride	T 50, 66.
C_3H_7Cl	Isopropyl chloride	T 25, 50, 66.
C_3H_7I	*n*—Propyl iodide	T 20.

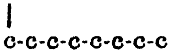
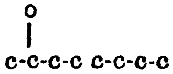
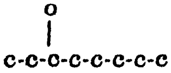
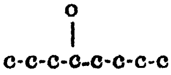
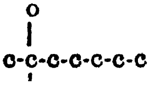
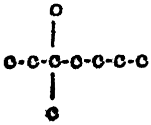
C_3H_7I	Isopropyl iodide	T 25.
$C_3H_7NO_2$	Propyl nitrite	T 22.
$C_3H_7NO_2$	Nitropropane	T 22.
$C_3H_7NO_3$	Propyl nitrate	T 22.
C_3H_8	Propane (liq.)	R 5.
C_3H_8O	Isopropyl alcohol	T 25.
$C_3H_8O_2$	1,2—Propylene glycol	T 46.
$C_3H_8O_3$	Glycerol	D 12; E 2; T 67.
C_3H_8S	Methyl ethyl sulphide	R 25.
C_3H_8S	Isopropyl mercaptan	T 25.
C_3H_9N	*n*—Propyl amine	T 19.
C_3H_9N	Isopropyl amine	T 25.
C_3H_9N	Trimethyl amine (liq.)	T 19.
$C_4H_4N_2$	Ethylene cyanide (melt.)	T 15.
$C_4H_5ClO_2$	β—Chlorocrotonic acid (sol.)	T 23.
$C_4H_5ClO_2$	β—Chloro isocrotonic acid (sol.)	T 23.
C_4H_5NS	Allyl isothiocyanate	T 56.
C_4H_6	Butadiene (liq.)	T 17.
$C_4H_6O_2$	Crotonic acid (melt. and sol.)	T 23.
$C_4H_6O_2$	Isocrotonic acid (sol.)	T 23.
$C_4H_6O_3$	Acetic anhydride	T 56.
$C_4H_7ClO_2$	Ethyl chloroacetate	T 46.
C_4H_7N	*n*—Butyronitrile	T 15.
C_4H_8	Ethyl ethylene (liq.)	T 10.
C_4H_8	Methyl cyclopropane (liq.)	T 13, 42.
C_4H_8O	1—Methyl allyl alcohol	T 10.
C_4H_8O	*n* – Butyraldehyde	T 46.
$C_4H_8O_2$	Dioxane	P 15.
$C_4H_8O_2$	Ethyl acetate	T 17, 81.
$C_4H_8O_2$	Methyl propionate	T 36.
C_4H_9Br	*n*—Butyl bromide	S 7.
C_4H_9Br	Isobutyl bromide	S 7.
C_4H_9Br	*sec.*—Butyl bromide	S 7.
C_4H_9Br	*tert.*–Butyl bromide	S 7; T 25.
C_4H_9Cl	*n*—Butyl chloride	T 20.
C_4H_9Cl	*tert.*—Butylchloride	T 25.
C_4H_9I	*n*—Butyl iodide	T 20.
C_4H_9I	*tert.*–Butyl iodide	T 25.
$C_4H_9NO_2$	*n*—Butyl nitrite	T 22.
$C_4H_9NO_2$	Nitrobutane	T 22.

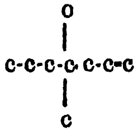
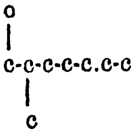
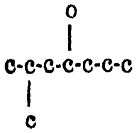
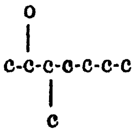
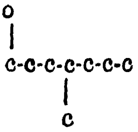
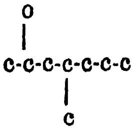
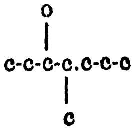
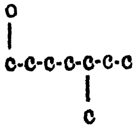
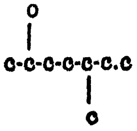
$C_4H_9NO_3$	*n*—Butyl nitrate	T 22.
C_4H_{10}	Butane (liq.)	R 5.
C_4H_{10}	Isobutane (liq.)	R 5.
$C_4H_{10}O$	Ether	Q 1.
$C_4H_{10}O$	*n*—Butyl alcohol	T 47.
$C_4H_{10}O$	*tert.*—Butyl alcohol	T 25, 47.
$C_4H_{10}S$	Diethyl sulphide	R 25; T 55, 63.
$C_4H_{10}SO_3$	Diethyl sulphite	R 25; T 48.
$C_4H_{10}S_2$	Ethyl disulphide	T 63.
$C_4H_{11}N$	Diethyl amine	T 19.
$C_5H_4O_2$	Furfural	T 43.
C_5H_5N	Pyridine	I 19; N 14; R 11; T 67.
	,, (mixt.)	T 67.
C_5H_8	Cyclo pentene	G 40.
C_5H_8	Dimethyl allene (unsym.)	S 3.
C_5H_8	Isoprene	T 17.
C_5H_8	Piperylene	T 17.
C_5H_8O	Dimethyl propargyl alcohol	T 11.
$C_5H_8O_2$	Methyl crotonate	T 23.
$C_5H_8O_2$	Methyl iso-crotonate	T 23.
C_5H_9N	*n*–Valeryl nitrile	T 15.
C_5H_9NS	Isobutyl isothiocyanate	T 15.
C_5H_{10}	Cyclopentane	R 39; T 18.
C_5H_{10}	Trimethyl ethylene	P 6.
C_5H_{10}	2—Methyl-3-butene	R 39.
C_5H_{10}	Propyl ethylene	T 10.
C_5H_{10}	1, 2-Dimethyl cyclopropane	T 42.
$C_5H_{10}O_2$	*n*-Butyl formate	T 46.
$C_5H_{11}Br$	*n*-Amyl bromide	S 7.
$C_5H_{11}Br$	Iso amyl bromide	S 7.
$C_5H_{11}Br$	*tert.*-Amyl bromide	T 25.
$C_5H_{11}Cl$	*tert.*-Amyl chloride	T 25, 46.
$C_5H_{11}N$	Piperidine	I 27.
$C_5H_{11}NO_2$	Nitropentane	T 22.
$C_5H_{11}NO_2$	Isoamyl nitrite	T 22.
$C_5H_{11}NO_3$	Amyl nitrate	T 56.
C_5H_{12}	Pentane	G 5; R 39.
$C_5H_{12}O$	*n*-Amyl alcohol	T 47.
$C_5H_{12}O$	Iso-amyl alcohol	G 17; T 47.
$C_5H_{12}O$	*d*-Amyl alcohol	T 47.

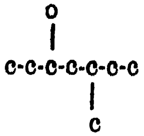
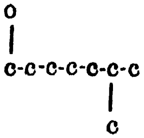
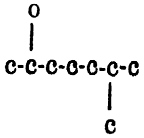
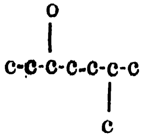
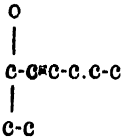
$C_5H_{12}O$	*sec.*-Amyl alcohol	T 47.
$C_5H_{12}O$	*tert.*-Amyl alcohol	T 25, 47.
$C_5H_{12}O$	Diethyl carbinol	T 47.
$C_6H_3Cl_3$	1, 2, 4-trichlorobenzene	T 46.
$C_6H_4BrNO_2$	*o*-Bromo nitrobenzene (melt.)	R 35.
$C_6H_4BrNO_2$	*m*-Bromonitrobenzene ,,	R 35.
$C_6H_4BrNO_2$	*p*-Bromonitrobenzene ,,	R 35.
$C_6H_4ClNO_2$	*o*-Chloronitrobenzene ,,	R 35.
$C_6H_4ClNO_2$	*m*-Chloronitrobenzene ,,	R 35.
$C_6H_4ClNO_2$	*p*-Chloronitrobenzene ,,	R 35.
$C_6H_4Cl_2$	*o*-Dichlorobenzene	T 45.
$C_6H_4Cl_2$	*m*-Dichlorobenzene	T 45.
$C_6H_4Cl_2$	*p*-Dichlorobenzene (melt.)	T 45.
C_6H_5Br	Bromobenzene	D 16; R 11.
C_6H_5Cl	Chlorobenzene	R 11.
C_6H_5ClO	Chlorophenol	T 46.
$C_6H_5ClO_2S$	Benzene sulfonic chloride	T 48.
C_6H_5I	Iodo benzene	T 20.
$C_6H_5NO_2$	Nitrobenzene	F 15; G 15; Q 9.
C_6H_6	Benzene	D 14, 16; E 13, 17; F 6, 8, 12, 14, 16, 18, 20, 21; G 2, 3, 5, 8, 11, 17, 18, 25; I 20; P 18; R 3, 11, 39; T 48.
	Benzene (mixt.)	F 7.
$C_6H_6O_3S$	Benzene sulfonic acid (melt.)	T 48.
C_6H_7N	Aniline	T 19, 30.
$C_6H_8O_4$	Di-metyl maleate	T 23.
$C_6H_8O_4$	Di-methyl fumarate (melt. and sol.)	T 23.
C_6H_{10}	Cyclohexene	R 39; T 46, 47.
C_6H_{10}	Propyl allene	S 3.
C_6H_{10}	*n*-Butyl acetylene	T 11.
C_6H_{10}	2, 3-Dimethyl butadiene	T 17.
$C_6H_{10}O$	Cyclohexanone	T 47.
$C_6H_{10}O_4$	Ethyl oxalate	T 56.
$C_6H_{10}S$	Allyl sulphide	T 55, 63.
$C_6H_{11}N$	Isocapronitrile	T 15.
C_6H_{12}	Cyclohexane	F 14, 18; G 5; I 20; R 39; T 13, 33, 41, 47.
C_6H_{12}	1-Hexene	T 10.

C_6H_{12}	Methyl cyclopentane	T 13.
C_6H_{12}	Butyl ethylene	P 10.
C_6H_{12}	1-Methyl-2-ethyl cyclopropane	P 10; T 42.
$C_6H_{12}N_4$	Hexamine	L 11.
	,, (sol.)	L 11.
$C_6H_{12}O$	Cyclohexanol	T 46, 47.
$C_6H_{12}O_2$	*n*-Propyl propionate	T 36, 46.
$C_6H_{12}O_2$	Isopropyl propionate	T 36.
$C_6H_{12}O_2$	*n*-Butyl acetate	T 46.
$C_6H_{12}O_6$	Glucose (sol.)	T 40.
$C_6H_{12}O_6$	Galactose (sol.)	T 40.
$C_6H_{12}O_6$	Fructose (sol.)	T 40.
$C_6H_{13}ClN_4$	Hexamine hydrochloride (sol.)	N 13.
C_6H_{14}	Hexane	E 21; T 38.
$C_6H_{14}O$	*n*-Propyl ether	T 36.
$C_6H_{14}O$	Isopropyl ether	T 36.
$C_6H_{14}S$	Propyl sulphide	T 63.
$C_6H_{15}N$	Triethylamine	T 19.
C_7H_5ClO	Benzoyl chloride	T 56.
C_7H_5NO	Phenyl *iso*-cyanate	T 15.
$C_7H_5NO_3$	*m*-Nitrobenzaldehyde (sol.)	T 22.
$C_7H_5NO_3$	*p*-Nitrobenzaldehyde ,,	T 22.
$C_7H_5NO_4$	*o*-Nitrobenzoic acid ,,	T 22.
$C_7H_5NO_4$	*m*-Nitrobenzoic acid ,,	T 22.
$C_7H_5NO_4$	*p*-Nitrobenzoic acid ,,	T 22.
C_7H_5NS	Phenyl *iso*-thiocyanate	T 15.
C_7H_6O	Benzaldehyde	E 20; T 43 .
C_7H_7Cl	Benzyl chloride	R 11.
C_7H_7Cl	*o*-Chlorotoluene	R 35; T 36.
C_7H_7Cl	*m*-Chlorotoluene	R 35; T 36.
C_7H_7Cl	*p*-Chlorotoluene	R 35; T 36.
$C_7H_7NO_2$	Phenyl nitromethane	T 22.
$C_7H_7NO_2$	*o*-Nitrotoluene	T 22, 36, 45.
$C_7H_7NO_2$	*m*-Nitrotoluene	T 22, 36, 45.
$C_7H_7NO_2$	*p*-Nitrotoluene (melt.)	T 22, 36, 45.
C_7H_8	Toluene	D 16; E 13, 15, 17; G 17, 18; T 48.
	,, (mixt.)	F 7.
$C_7H_8O_3S$	Toluene *p*-sulphonic acid (sol.)	T 48.
C_7H_9N	Methyl aniline	T 30.

C_7H_9N *o*-Toluidine T 30, 45.
C_7H_9N *m*-Toluidine T 45.
C_7H_9N *p*-Toluidine (melt.) T 45.
C_7H_{12} Butyl allene S 3.
C_7H_{12} *n*-Amyl acetylene T 11.
$C_7H_{12}O$ *o*-Methyl cyclohexane T 47.
$C_7H_{12}O$ *m*-Methyl cyclohexane T 47.
$C_7H_{12}O$ *p*-Methyl cyclohexane T 47,
$C_7H_{12}O_4$ Ethyl malonate (sol.) T 31.
C_7H_{14} 1-Heptene P 10; T 10.
C_7H_{14} Methyl cyclohexane T 13, 33, 47.
C_7H_{14} Cycloheptane T 13.
C_7H_{14} 1-Methyl 2-propyl cyclopropane T 42.
$C_7H_{14}O$ Heptaldehyde T 43.
$C_7H_{14}O$ *o*-Methyl cyclohexanol T 47.
$C_7H_{14}O$ *m*-Methyl cyclohexanol T 47.
$C_7H_{14}O$ *p*-Methyl cyclohexanol T 47.
$C_7H_{14}O_2$ *n*-Butyl propionate T 36.
$C_7H_{14}O_2$ Isobutyl propionate T 36.
C_7H_{16} Heptane T 14.
C_8H_5Cl 1-Chloro phenyl acetylene T 11.
C_8H_6 Phenyl acetylene T 11.
C_8H_7N *o*-Tolunitrile T 15.
C_8H_7N Benzyl nitrile T 18.
C_8H_7NS *p*-Tolyl isothiocyanate T 15.
C_8H_8 Phenyl ethylene T 10, 41.
C_8H_{10} *o*-Xylene D 16.
C_8H_{10} *m*-Xylene D 16.
C_8H_{10} *p*-Xylene D 16.
,, (mixt.) G 18.
$C_8H_{10}O$ 1, 2, 3—Xylenol (melt.) T 24,
$C_8H_{10}O$ 1, 3, 4—Xylenol ,, T 24.
$C_8H_{10}O$ 1, 2, 5—Xylenol ,, T 24.
$C_8H_{10}O$ 1, 2, 4—Xylenol T 24.
$C_8H_{10}O$ 1, 3, 5—Xylenol (melt.) T 24.
$C_8H_{10}O$ 1, 2, 6—Xylenol (melt. and sol.) T 24.
$C_8H_{10}O$ *o*-Cresyl methyl ether T 36.
$C_8H_{10}O$ *m*-Cresyl methyl ether T 36.
$C_8H_{10}O$ *p*-Cresyl methyl ether T 36.
$C_8H_{11}N$ 1, 2, 3—Xylidine T 24

$C_8H_{11}N$	1, 3, 4—Xylidine (sol.)	T 24.
$C_8H_{11}N$	1, 2, 5—Xylidine	T 24.
$C_8H_{11}N$	1, 2, 4—Xylidine	T 24.
$C_8H_{11}N$	1, 3, 5—Xylidine	T 24.
$C_8H_{11}N$	1, 2, 6—Xylidine	T 24, 30.
$C_8H_{11}N$	Dimethyl aniline	T 30.
$C_8H_{12}O_4$	Diethyl maleate	T 23, 29.
$C_8H_{12}O_4$	Diethyl fumarate	T 23, 29.
C_8H_{14}	*n*-Hexyl acetylene	T 11.
C_8H_{14}	Methyl *n*-amyl acetylene	T 11.
$C_8H_{14}O_2$	Cyclohexyl acetate	T 47.
C_8H_{16}	*n*-Octylene	T 10.
C_8H_{16}	Cyclooctane	T 13.
C_8H_{16}	Methyl cycloheptane	T 13.
C_8H_{16}	*o*-Dimethyl cylohexane	T 33.
C_8H_{16}	*m*-Dimethyl cyclohexane	T 33.
C_8H_{16}	*p*-Dimethyl cyclohexane	T 33.
$C_8H_{16}O_2$	*n*-Amyl propionate	T 36.
$C_8H_{16}O_2$	Iso-amyl propionate	T 36.
C_8H_{18}	Octane	I 20; T 14.
$C_8H_{18}O$	Octyl alcohol  c-c-c-c-c-c-c-c	T 14, 47.
$C_8H_{18}O$	,,  c-c-c-c c-c-c-c	T 14, 47.
$C_8H_{18}O$	,,  c-c-c-c-c-c-c-c	T 14.
$C_8H_{18}O$	,,  c-c-c-c-c-c-c-c	T 14.
$C_8H_{18}O$	,,  c-c-c-c-c-c-c	T 14.
$C_8H_{18}O$	,,  c-c-c-c-c-c-c	T 14.

$C_8H_{18}O$	,,	 $c\text{-}c\text{-}c\text{-}\overset{o}{\underset{c}{c}}\,c\text{-}c\text{-}c$	T 14.
$C_8H_{18}O$	,,	 $\overset{o}{c}\text{-}\underset{c}{c}\text{-}c\text{-}c\text{-}c.c\text{-}c$	T 14.
$C_8H_{18}O$	,,	 $c\text{-}\underset{c}{c}\text{-}c\text{-}\overset{o}{c}\text{-}c\text{-}c\text{-}c$	T 14.
$C_8H_{18}O$	,,	 $c\text{-}\overset{o}{c}\text{-}\underset{c}{c}\text{-}c\text{-}c\text{-}c\text{-}c$	T 14.
$C_8H_{18}O$	,,	 $\overset{o}{c}\text{-}c\text{-}c\text{-}\underset{c}{c}\text{-}c\text{-}c\text{-}c$	T 14.
$C_8H_{18}O$	,,	 $c\text{-}\overset{o}{c}\text{-}c\text{-}\underset{c}{c}\text{-}c\text{-}c\text{-}c$	T 14.
$C_8H_{18}O$	,,	 $c\text{-}c\text{-}\overset{o}{c}\text{-}\underset{c}{c}.c\text{-}c\text{-}c$	T 14.
$C_8H_{18}O$	,,	 $\overset{o}{c}\text{-}c\text{-}c\text{-}c\text{-}\underset{c}{c}\text{-}c\text{-}c$	T 14.
$C_8H_{18}O$	,,	 $c\text{-}\overset{o}{c}\text{-}c\text{-}c\text{-}\underset{c}{c}\text{-}c.c$	T 14.

$C_8H_{18}O$	,,	 $c\text{-}c\text{-}\overset{o}{\overset{\vert}{c}}\text{-}c\text{-}\underset{\underset{c}{\vert}}{c}\text{-}c\text{-}c$	T 14.
$C_8H_{18}O$	,,	 $\overset{o}{\overset{\vert}{c}}\text{-}c\text{-}c\text{-}c\text{-}c\text{-}\underset{\underset{c}{\vert}}{c}\text{-}c$	T 14..
$C_8H_{18}O$	,,	 $c\text{-}\overset{o}{\overset{\vert}{c}}\text{-}c\text{-}c\text{-}c\text{-}\underset{\underset{c}{\vert}}{c}\text{-}c$	T 14.
$C_8H_{18}O$	,,	 $c\text{-}c\text{-}\overset{o}{\overset{\vert}{c}}\text{-}c\text{-}c\text{-}\underset{\underset{c}{\vert}}{c}\text{-}c$	T 14.
$C_8H_{18}O$	,,	 $\overset{o}{\overset{\vert}{\underset{\underset{c\text{-}c}{\vert}}{c}}}\text{-}c\text{-}c\text{-}c.c\text{-}c$	T 14.
$C_8H_{18}S$	*n*-Butyl sulphide		T 63.
$C_8H_{18}S$	Isobutyl sulphide		T 63.
C_9H_7N	Quinoline		T 6.
C_9H_8	Methyl phenylacetylene		T 11.
C_9H_8	Phenyl allylene		T 11.
C_9H_9Br	2-Bromo-2-benzyl ethylene		T 41.
$C_9H_9ClO_2$	Benzyl chloroacetate		T 46.
C_9H_{10}	Benzyl ethylene		T 10, 41.
C_9H_{10}	Isoallyl benzene		T 41.
C_9H_{10}	Phenyl trimethylene		T 41,42.
$C_9H_{10}O_2$	Ethyl benzoate		T 31.
$C_9H_{10}O_2$	Benzyl acetate		T 46.
$C_9H_{14}O$	Methyl octionate		T 11.
$C_9H_{16}O_2$	Cyclohexyl propionate		T 47.
C_9H_{18}	Heptylethylene		T 10.
C_9H_{18}	2-Methyl-1-octene		T 84.
C_9H_{18}	2-Methyl-2-octene		T 84.
C_9H_{18}	Methyl cyclooctane		T 18.

$C_{10}H_7Br$	2-Bromonaphthalene	T 20.
$C_{10}H_{10}$	1, 4-Dihydronaphthalene (melt.)	T 9.
$C_{10}H_{10}O_2$	Safrol	T 46.
$C_{10}H_{12}$	1,2,3,4-Tetrahydronaphthalene	T 5.
$C_{10}H_{14}$	*p*-Cymene	T 46.
$C_{10}H_{14}O$	Carvone	T 7.
$C_{10}H_{15}N$	Diethylaniline	T 30.
$C_{10}H_{16}$	Carene	T 47.
$C_{10}H_{16}$	Thujene	T 47.
$C_{10}H_{16}$	*d*-Pinene	H 4 ; R 19 ; T 4, 47.
$C_{10}H_{16}$	*l*-Pinene	H 4 ; R 19 ; T4, 47.
$C_{10}H_{16}$	Limonene	T 4, 41.
$C_{10}H_{16}$	Sabinene	T 4, 47.
$C_{10}H_{16}O$	Pulegon	T 7.
$C_{10}H_{16}O$	Carvenone	T 7.
$C_{10}H_{16}O$	Thujone	T 7.
$C_{10}H_{16}O$	Fenchone	T 7
$C_{10}H_{16}O$	Citral	T 7.
$C_{10}H_{18}$	Menthene	T 4, 41.
$C_{10}H_{18}$	Pinane	T 4.
$C_{10}H_{18}$	Sabinane	T 4.
$C_{10}H_{18}$	Decahydronaphthalene	T 5.
$C_{10}H_{18}O$	Menthone	T 7.
$C_{10}H_{18}O$	Terpineol	T 7.
$C_{10}H_{18}O$	Eucaliptol	T 7.
$C_{10}H_{18}O$	Citronellal	T 7.
$C_{10}H_{18}O$	Linalol	T 7.
$C_{10}H_{18}O$	Geraniol	T 7.
$C_{10}H_{20}$	Menthane	T 4.
$C_{10}H_{20}$	3-Methyl-3-nonene	T 34
$C_{10}H_{20}$	2-Ethyl-1-octene	T 34.
$C_{10}H_{20}$	3-Methyl-2-nonene	T 34.
$C_{10}H_{20}O$	Citronellol	T 7, 34.
$C_{10}H_{20}O$	Rhodinol	T 34.
$C_{10}H_{22}O$	*n*-Amyl ether	T 36.
$C_{10}H_{22}O$	Isoamyl ether	T 36.
$C_{11}H_7NO$	2-Naphthyl isocyanate	T 15.
$C_{11}H_{10}$	3-Phenyl acetylene propylene	T 10.
$C_{12}H_{10}$	Diphenyl (melt.)	D 16; P18.
$C_{12}H_{10}O$	Phenyl ether	D 16; T 19.

$C_{12}H_{10}S_2$	Diphenyl disulphide	D 16.
$C_{12}H_{11}N$	Diphenyl amine	T 19.
$C_{12}H_{22}O_{11}$	Saccharose (sol.)	T 40, 51, 67
$C_{12}H_{24}O_{12}$	Maltose ,,	T 40.
$C_{13}H_{10}ClN$	*p*-Chlorobenzylidene aniline (sol.)	T 8.
$C_{13}H_{10}ClN$	Benzalchloraniline (sol.)	T 8.
$C_{13}H_{11}N$	Benzylidene aniline ,,	T 8.
$C_{13}H_{12}$	Diphenyl methane	R 14.
$C_{13}H_{20}O$	Ionone	T 28.
$C_{14}H_{10}$	Tolane (melt.)	R 14.
$C_{14}H_{12}$	*cis*-Stilbene	R 14.
$C_{14}H_{12}$	*trans*-Stilbene	R 14.
$C_{14}H_{13}NO$	Benzoyl p-toluidine (sol.)	T 8.
$C_{14}H_{14}$	Dibenzyl (melt.)	R 14.
$C_{15}H_{14}$	1.2-Diphenyl cyclopropane	T 42.
$C_{18}H_{32}O_{16}$	Raffinose (sol.)	T 40.
$C_{20}H_{28}$	*α*-Carotin ,,	T 28.
$C_{20}H_{28}$	*β*-Carotin ,,	T 28.
$C_{40}H_{56}O_2$	Xanthophyll ,,	T 28.
	Lycopin	T 28.
	Poly-styrol	R 36.

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36

Magnetic Birefringence in Liquid Mixtures

By

S. W. CHINCHALKAR.

(Received for publication, 10th October, 1932.)

ABSTRACT.

The magnetic birefringence in liquid mixtures is known to show large deviations from theoretically expected values, and no explanation of these variations has so far been given. In order to investigate into this problem, magnetic birefringence in twenty-one binary liquid mixtures has been studied. The double refraction was estimated by measuring the shift of the dark band in Rayleigh's bent glass plate compensator. The results (Tables and curves 1 to 21) which are consistent with those of the previous workers, have the following chief features:—Curves for aniline, benzene, and toluene are concave towards the axis of concentration (in partial volumes), those for ethyl benzene, bromo-benzene and chlorobenzene are nearly straight, while those for CS_2 and nitrobenzene are convex, the gradual variation in the curvatures following the above order of the liquids; the different liquids mixed with the above ones change the curvatures slightly, keeping the essential features the same; there is an asymmetry in the curves for aniline. The curves to be expected on Langevin's theory are also drawn.

The experimental curves are correlated with the existing data on (1) temperature variation of magnetic birefringence, (2) temperature variation of molecular optical anisotropy and (3) optical anisotropy in the vapour and liquid states. From the striking correspondence between these different data, it is suggested that the variation in the effective optical anisotropy of the molecules with dilution is at least one, and probably the main, cause of the deviations observed in the birefringence in mixtures. The physical interpretation of the variations is discussed.

1. *Introduction.*

Magnetic birefringence in mixtures of organic liquids has been studied by Cotton and Mouton[1] and by Szivessy and Richartz.[2] The substances used by them were two nitro-compounds (nitro-benzene and nitro-toluene) and two halogen compounds (α-chloro-naphthalene and α-bromo-naphthalene), these being mixed with different organic liquids, both aliphatic and aromatic. These authors found that in almost all the cases the experimental values differed much from those to be expected on theoretical grounds, and no explanation or correlation of these departures has so far been put forward. The present investigation was undertaken as an attempt to try to understand the cause of these variations and to see if any light could be thrown on them by extending the available information with further experiments and by trying to correlate the observed variations with other existing data about these substances.

2. *The Law of Mixtures on Langevin's Theory.*

The Cotton-Mouton constant C of magnetic birefringence is defined by

$$C=\frac{n_p-n_s}{\lambda H^2} \qquad \dots \qquad \dots \qquad \dots \qquad \text{(i)}$$

where n_p and n_s are the refractive indices of the liquid for light vibrations parallel and perpendicular to the applied magnetic field, λ the wave length of light used and H the strength of the magnetic field. Langevin's theory of magnetic birefringence assumes a magnetic as well as an optical anisotropy for the molecules of the liquid exhibiting the birefringence.

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[1] Cotton and Mouton, C.R., *156*, 1456 (1913); Ann. Chim. Phys., *30*, 321 (1913).

[2] Szivessy and Richartz, Ann. der Phys., *86*, 3

Due to the magnetic anisotropy, the molecules tend to orientate themselves when placed in an external magnetic field, thermal agitations opposing, and this tendency to orientate makes the liquid doubly refracting to a small extent due to the optical anisotropy of the molecules. In calculating[3] an expression for C on this theory, the number of molecules per unit volume which will orientate with their axes having a definite inclination to the external magnetic field is calculated according to the Maxwell-Boltzmann expression, and thence the double refraction in the medium due to this orientation. The effect is then averaged over all the molecules. In the case of mixtures of liquids[4] the same treatment is given to the molecules of each kind separately, and the average optical moments contributed by a molecule of each kind per unit field of the incident light wave when the light vibrations are parallel and perpendicular to the magnetic field applied, are calculated. Let these be M'_p and M'_s for the molecules of kind 1, M''_p, M''_s, for kind 2 and so on. If $\nu_1, \nu_2, \ldots\ldots$ are the numbers of molecules of 1st, 2nd...kind per unit volume of the mixture, the moments P_p and P_s per unit volume of the mixture are

$$P_p = \nu_1 M'_p + \nu_2 M''_p + + \ldots = \frac{\nu_1}{N_1} . N_1 M'_p + \frac{\nu_2}{N_2} . N_2 M''_p + + \qquad \text{(ii)}$$

$$P_s = \nu_1 M'_s + \nu_2 M''_s + + \ldots = \frac{\nu_2}{N_2} N_1 M'_s + \frac{\nu_2}{N_2} N_2 M''_s + + . \qquad \text{(iii)}$$

where N_1, N_2,... are the number of molecules per unit volume in pure liquids. According to the Lorentz formula we have the relations

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[3] Debye, Handbuch der Radiologie, Bd. VI, p. 769.

[4] Bergholm—Archiv. f. Mat. Astr. and Fys., Bd. 12, No. 3 (1917).
Szivessy—Zeit. f. Phys., 7, 285 (1921).
Bergholm has calculated the relation for the electrical double refraction. The effect of permanent electric moments was not taken note of when he gave the formula and the results are valid for the magnetic case also.

$$\left.\begin{aligned} &\frac{n_p^2-1}{n_p^2+2}=\tfrac{4}{3}\pi P_p \;; \quad \frac{n'^2_p-1}{n'^2_p+2}=\tfrac{4}{3}\pi N_1 M'_p \;; \quad \text{etc.} \\ &\frac{n_s^2-1}{n_s^2+2}=\tfrac{4}{3}\pi P_s \;; \quad \frac{n'^2_s-1}{n'^2_s+2}=\tfrac{4}{3}\pi N_1 M'_s \;; \quad \text{etc.} \end{aligned}\right\} \qquad \text{(iv)}$$

where n's represent the refractive indices. Subtracting (iii) from (ii) and using eqns. (iv), and remembering that n_p's and the corresponding n_s's are nearly equal, we get

$$\frac{(n_p-n_s)n}{(n^2+2)^2}=\frac{v_1}{N_1}\;\frac{(n'_p-n'_s)n_1}{(n_1{}^2+2)^2}+\frac{v_2}{N_2}\;\frac{(n''_p-n''_s)n_2}{(n_2{}^2+2)^2}++ \qquad \text{(v)}$$

where n, n_1,...represent the mean refractive indices. If m_1, m_2, etc., are the number of grams of liquids 1, 2,...per c.c. of the mixture, and if d_1, d_2...are their densities, the partial volumes v_1 $\left(=\frac{m_1}{d_1}\right)$, v_2 $\left(=\frac{m_2}{d_2}\right)$......of the liquids in the mixture are equal to ν_1/N_1, ν_2/N_2 .....occurring in (v). From this and using (i), (v) reduces to

$$C\frac{n}{(n^2+2)^2}= C_1v_1\frac{n_1}{(n_1^2+2)^2} + C_2v_2\frac{n_2}{(n_2{}^2+2)^2}+\ldots \qquad \text{(vi)}$$

where C is the Cotton-Mouton constant of the mixture, and C_1 C_2,......are those of the liquids 1, 2,......For binary mixtures, with one component of the mixture having a negligible magnetic birefringence ($C_2=0$), the above reduces to

$$C=C_1v_1\frac{n_1}{(n_1{}^2+2)^2}\cdot\frac{(n^2+2)^2}{n} \qquad \text{(vii)}$$

3. *The Compensator.*

In his previous investigations[5] on magnetic birefringence, the author had used the stained glass half-shade compensator for the measurement of the double refraction. Since in the present case, the birefringence to be measured was not so small as in the previous cases, a more quick and handy method was resorted to. The bent glass plate described by Lord Rayleigh [6] was here used to measure the double refraction. Ordinary glass under pressure (or tension) is known to behave like a negetive (positive) uniaxial crystal with the axis along the direction of pressure (tension) and the birefringence can be taken to be proportional to the pressure (or tension). In a long thin glass plate bent in its own plane, the different layers above and below the neutral axis will behave like a series of uniaxial positive and negative crystals respectively, with their axes parallel to the neutral axis. Also since the strain in the different layers is proportional to their distances from the neutral axis, the birefringence produced by the layers will also be proportional to their distances from it. If a beam of plane polarised light with its direction of vibration inclined at 45° to the neutral axis is allowed to pass through the plate and then examined with a crossed analysing nicol and a telescope focussed on the plate, there will be seen in the field of view a dark band corresponding to the light passing through the neutral axis which passes unmodified through the plate and is quenched by the analyser. On either side of this dark band the light will not be quenched as it is elliptically polarised due to the double refraction produced by those parts of the bent plate, the sense of the ellipticity on the two sides of the band being opposite. If now the incident light is elliptically polarised, having a phase retardation δ_1 between light vibrations parallel and perpendicular to the neutral axis, the light will be made plane polarised by that layer of the plate which produces a retardation equal and opposite to δ_1, the dark band shifting to that place. From what has been said above, it can be seen that the sign and magnitude of the shift will thus determine the sign and magnitude of the phase difference between the incident light vibrations parallel and perpendicular to the dark band, so long as the bending moment applied to the ends of the plate is unchanged. Thus all that is necessary to measure the relative birefringence in the case of mixtures with different concentrations for a given pair of liquids is to measure the shifts produced by these mixtures, keeping the bending moment of the plate constant.

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[5] Ind. Jour. Phys., Vol. VI, pp. 165 and 581; Vol. VII, p. 317.

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[6] Rayleigh, Phil. Mag., 4, 680 (1902).
Szivessy, Handbuch der Physik., Bd. 19, p. 949.

For a given bending moment a strong source of light will be preferable in order that the parts of the plate very near to the neutral axis should restore an appreciable amount of light, making the dark band narrow. The range of the instrument as also the sharpness of the dark band can be increased by increasing the bending moment, when, however, the shift for a given birefringence, *i. e.*, the sensitivity, will become smaller. On the other hand, the use of too low a bending moment for increasing the sensitivity makes the band broad and diffuse, introducing an uncertainty in its location. Hence the proper amount of bending for a series of mixtures of a given pair of liquids can be chosen by considering all these factors, *viz.*, the strength of the course of light available, the breadth of the beam, the shift for a given birefringence and the range of the values required to be measured.

The actual strip of glass used was about 10·5 cms × 1·cm. bent in its own plane by the pressure applied at its ends. The thickness of the plate was about 1·5 mm. Suitable thin rubber pads were given below to ensure an even distribution of pressure at the points of application.

4. *Experimental.*

The other experimental arrangement was the same as in the author's earlier work.[7] The strong source of light was a

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[7] S. W. Chinchalkar, Ind. Jour. Phys., 6, 165 (1931).

1000 c. p. pointolite lamp, the light from which was condensed and collimated before passing through the polariser of which the principal direction of vibration was inclined at 45° to the horizontal. The direction of the magnetic field as well as the neutral axis was horizontal. The liquid mixtures were kept in stoppered glass tubes 33 cms. long with thin plane windows sealed to the ends. The tubes were kept in an equally long gap of the special electromagnet.[8] In all cases, a current of 11 amps. was used in the electromagnet giving a field of about 24000 gauss, except in the case of nitrobenzene where a lower current of about 4 amps. was found quite sufficient to give a large shift, of the same order as in the other liquids. The shift of the dark band was measured by means of an Adam Hilger micrometer eye-piece with which the observing telescope was fitted. The position of the centre of the band could be located to within one division of the micrometer scale. The mean of six or more readings was taken as the shift in each case. Considering the order of the shifts of the dark band in the various mixtures as given later (Tables 1 to 21) under results, one can get an idea of the sensitivity of the method. The deviations of the experimental values from the theoretical ones are far too large to be masked by, or even appreciably affected by, the errors in measurement, as can easily be seen from the curves. Test values were consistent when taken with different pure liquids and a comparison of the curves for nitrobenzene-CCl_4 mixtures with the same mixture investigated by Cotton and Mouton, shows that the two values agree very well (see Fig. 13).

The liquids used were of Kahlbaum's or Merck's manufacture. In most cases, one liquid was chosen to possess a high value of magnetic birefringence and the other almost negligible, so that from the birefringence point of view the one may be said to have been diluted by the other. The "diluents" were mostly carbon tetrachloride (Merck's extra pure or "Kahlbaum's") and cyclohexane, and in a few cases acetone. The cyclohexane used was tested with a sensitive half shade compensator and found to exhibit a feeble positive birefringence of the value of +0·03 as compared with +100 for nitrobenzene. Comparing this with the portion of the benzene-cyclohexane curve (Fig. 2) at infinite dilution and taking −0·5 as the value of magnetic birefringence for pure cyclohexane,[9] it is found that the sample of cyclohexane used contained about 1% of benzene as impurity.

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[8] M. Ramanadham, Ind. Jour. Phys., 4, 15 (1929).

According to equation (vii) the concentrations of the mixtures should be expressed in terms of the partial volumes of one component. If V_1 and V_2 c.cs. of two liquids on mixing give V as the volume of the mixture, the partial volume v_1 $(=V_1/V)$ of liquid 1 is equal to $\frac{v_1}{v_1+v_2}$ provided the volume change produced on mixing is negligible. The diluents in most of our cases being non-polar, the volume changes were expected to be small. The volume changes in the mixtures proposed to be investigated were found out from available data (*e.g.*, International Critical Tables, Vol. III). It was seen that in most of the mixtures the maximum changes were of the order of 0·2 to 0·3 per cent. or even less, which were well within the accuracy of the measurement of the shift. It would have been indeed superfluous to take account of the changes in these cases. Where the changes were larger than these, due corrections were made, the mixtures being in all cases made by weights.

5. *Results.*

The results for the twenty-one mixtures studied are given in the tables (1 to 21) at the end of the paper. The

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[9] Scherer, C. R., *192*, 1223 (1931).

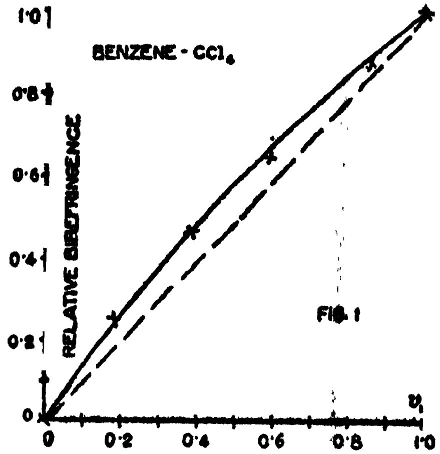

FIG. 1

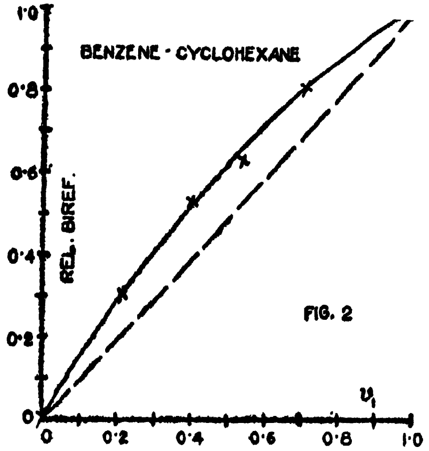

FIG. 2

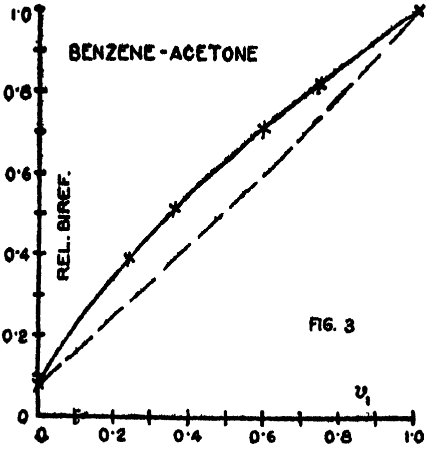

FIG. 3

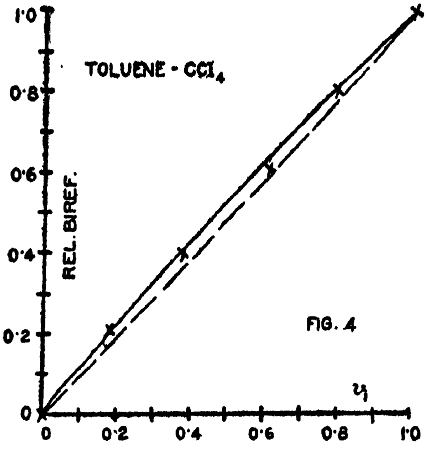

FIG. 4

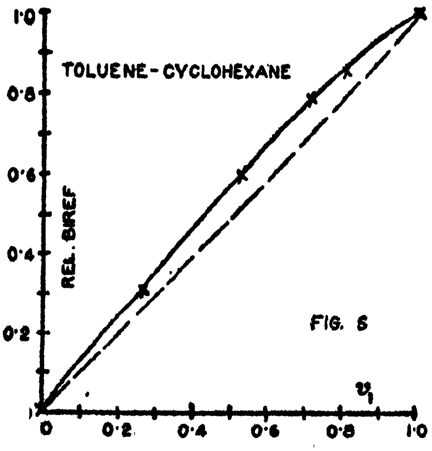

FIG. 5

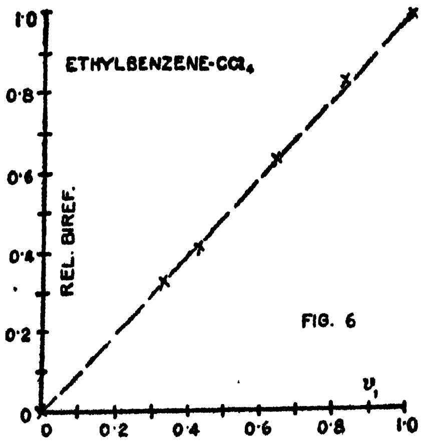

FIG. 6

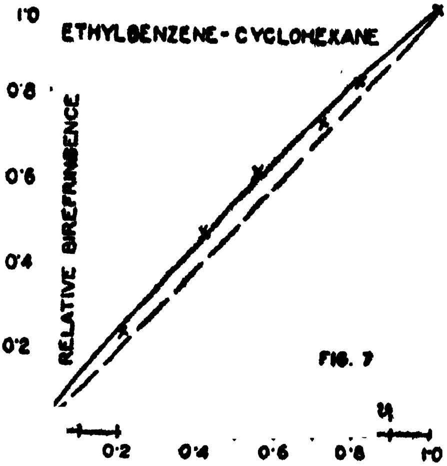

FIG. 7

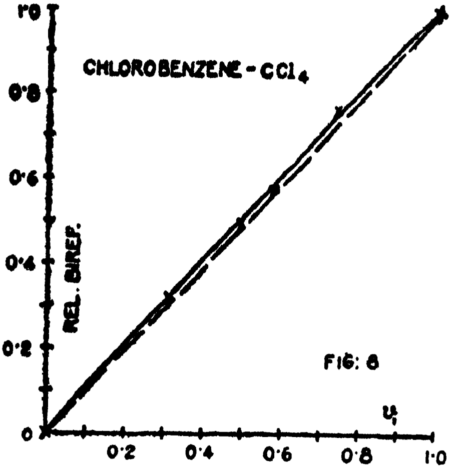

FIG: 8

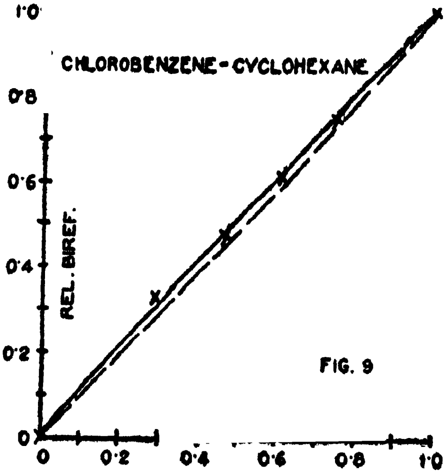

FIG. 9

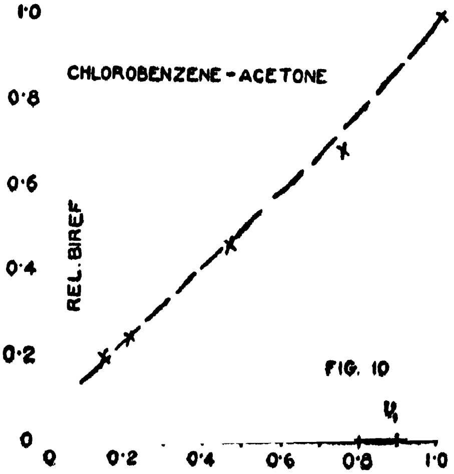

FIG. 10

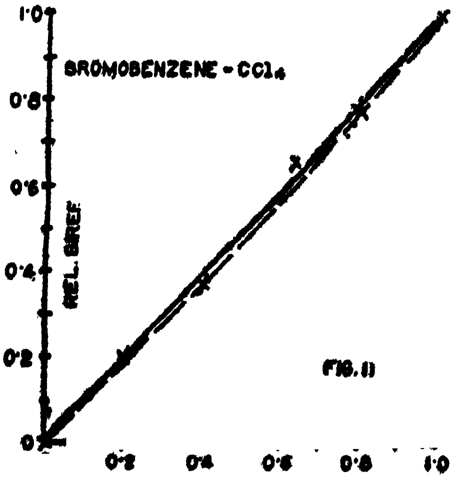

FIG. 11

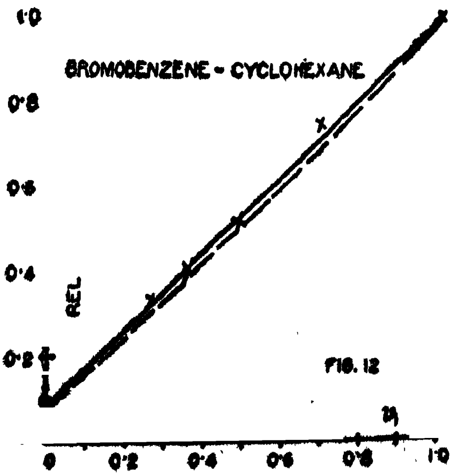

FIG. 12

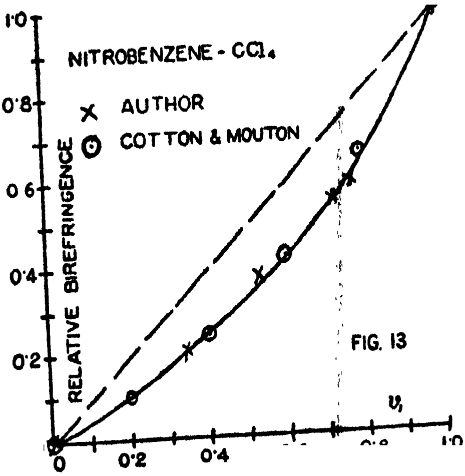

FIG. 13

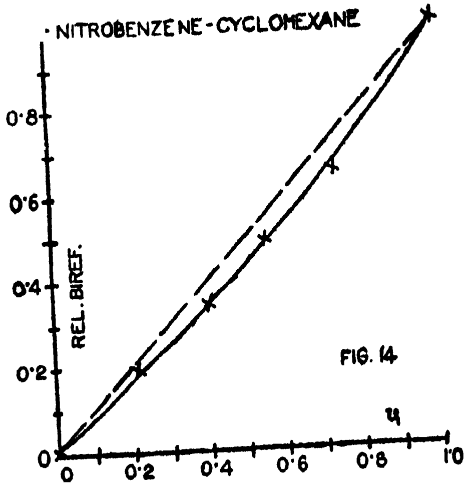

FIG. 14

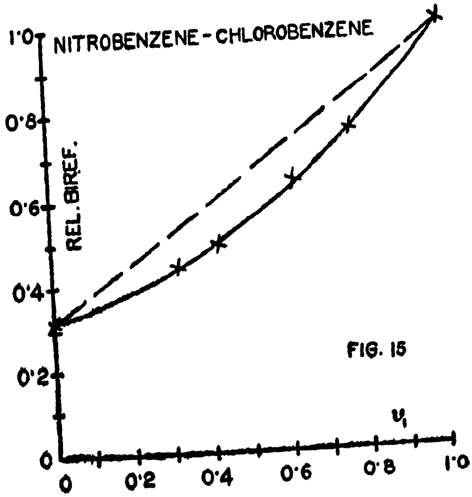

FIG. 15

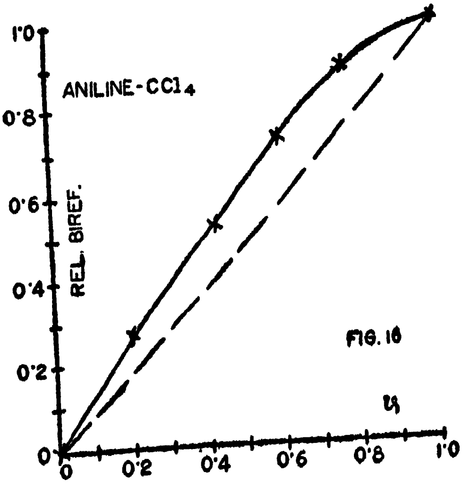

FIG. 16

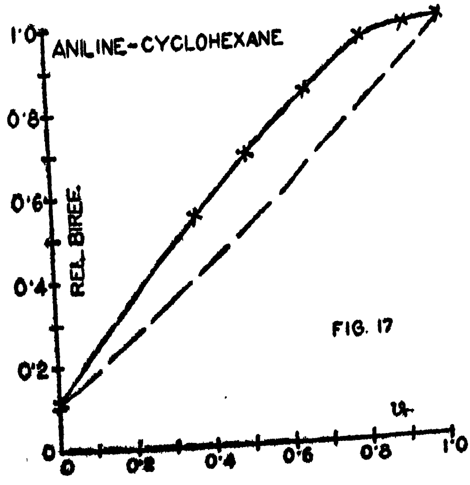

FIG. 17

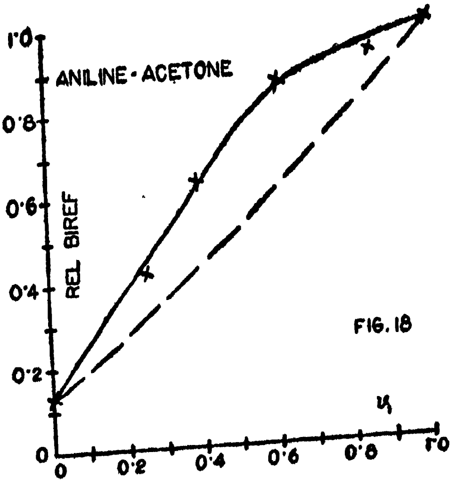

FIG. 18

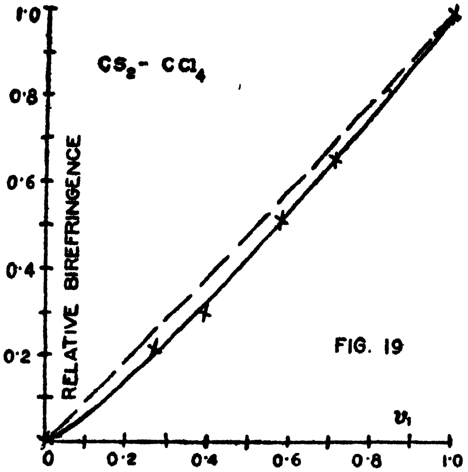

FIG. 19

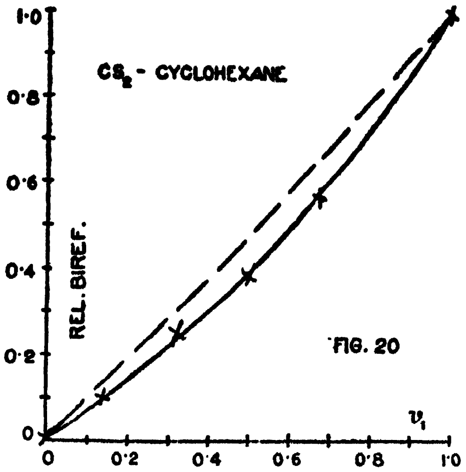

FIG. 20

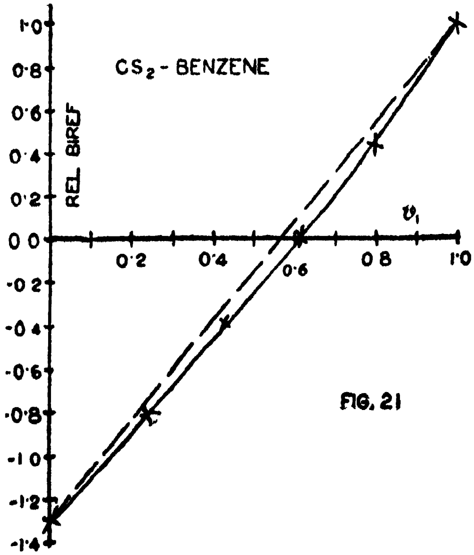

FIG. 21

first column of the tables gives the partial volumes of the first-named liquid in the pair constituting the mixtures; the second column gives the shift of the dark band in micrometer screw divisions, it being proportional to the birefringence; the third column gives the relative birefringence assuming the value unity for the mixture with partial volume 1. In the curves this relative birefringence is plotted against the partial volumes. This secures the same relative value of maximum birefringence for all the mixtures; and a glance at the curves gives an idea of the relative deviations for the different cases. The curves theoretically expected (eq. vii) are drawn by broken lines. The refractive index n of the mixture used to calculate the theoretical values was calculated from the concentrations of the mixtures by Lorentz formula. It was verified from available data of refractive indices of mixtures that the use of the actual experimental value of n for a given mixture instead of that calculated from the Lorentz formula does not alter the factor $\left\{\frac{(n^2+2)^2}{n} \cdot \frac{n_1}{(n_1^2+2)^2}\right\}$ occurring in equation (vii) to an appreciable extent. The theoretical curves vary only slightly from a linear relation; hence the theoretial values have not been given in the tables.

6. *Discussion.*

On examining the different curves, it is seen that (*a*) mixtures of benzene, toluene and aniline exhibit curves concave towards the axis of concentration, those of nitrobenzene and carbon disulphide are convex, while those of chloro- and bromo-benzene and ethyl-benzene more or less agree with the theoretical curves and are almost straight; (*b*) any of the "diluents" used keeps the essential nature of the curve of a given liquid the same, though in several cases it is found that when cyclohexane is used as a diluent, the curves are a little less convex (or more concave) towards the concentration axis than when carbon tetrachloride was used; (*c*) a gradual diminution is found in the concavity of the curves towards the concentration axis in the benzene derivatives in the following order:—benzene, toluene, ethylbenzene, bromobenzene, chlorobenzene and nitrobenzene, the change being rather sudden in the case of nitrobenzene ; (*d*) there is a pronounced asymmetry in the curves of aniline (Figs. 16-18), the rate of diminution of magnetic birefringence with dilution being very small up to about 75% volume concentration, and thereafter increasing markedly. On examining the results of earlier workers, one finds that many of these essential features are to be seen in their work also. Thus, Cotton and Mouton[1] found the nitrobenzene curves convex when ethyl school, acetone and dibromoethane were used as diluents, agreeing with (*b*) above. Results of Szivessy and Richartz[2] show that curves for nitrobenzene and nitrotoluene were fairly convex, but those with chloronaphthalene (analogous to our chlorobenzene) have very little curvature, being almost straight and close to the theoretical curves ; this agrees with our (*c*).

According to Langevin's theory of magnetic birefringence the molecules of the liquid are optically as well as magnetically anisotropic. Apart from their anisotropies, in a dense fluid like a liquid, the behaviour of the molecules would be modified by the influence of the neighbouring molecules also. Thus, if the molecules are electrically polar, the phenomena of molecular association would be a prominent feature of the intermolecular influences. Even in non-polar substances, Raman and Krishnan[10] have shown that the effect of the non-symmetrical shape of the molecules results in the polarisation field at a molecule due to the surrounding ones becoming anisotropic. Without going for the present into the cause and nature of the influence of the neighbouring molecules, we can take it that these do modify the observed properties of a given molecule. As a result of mixing some foreign liquid, the given liquid is rarefied, and the influence of molecules of its own kind on a given molecule becomes smaller. Thus, for example, it is known that polar association tends to break up by dilution. A change in the physical conditions of a liquid which produces effects similar to " dilution " is the heating of a liquid and the ultimate case of vaporisation. The intermolecular influences are modified by heating, on the one hand, by a change of volume so that each molecule gets more space for itself, and on the other, if there is any sort of a regular order in a liquid as due to polar association or due to other forces like the " van der Waal forces," this order tends to be destroyed by the increasing thermal agitation. It would therefore be instructive to compare the temperature variation of those properties of liquids which are related to magnetic birefringence, with the variations of magnetic birefringence in mixtures. In making these comparisons and in all the discussions to follow, the following remark about the curvatures will always be remembered. From the point of view of Langevin's theory, the interpretation of the different curvatures is that for those cases where the concentration-birefringence curve is more convex (or concave) towards the concentration axis than the theoretical curve, the effective anisotropy of the molecules of the liquid, either optical or magnetic or both, is decreased (or increased) when the liquid is " diluted."

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[10] *e. g.*, Raman and Krishnan, Phil. Mag., *5*, 498 (1928); Proc. Roy, Soc., A., *117*, 1 (1927).

7. *Relation with Temperature Variation of Magnetic Birefringence.*

Let us take first the variation of magnetic birefringence itself with temperature. According to Langevin's theory, the absolute temperature T, the refractive index n, the density d and the Cotton-Mouton constant C are connected by the relation

$$C = \frac{d(n^2+2)^2}{nT}k \qquad \ldots \quad \text{(viii)}$$

where n is the number of molecules per c. c. For the case of a perfect gas (or vapour very approximately) this reduces to

$$\delta_{gas} = \frac{10r}{6-7r} \tag{xii}$$

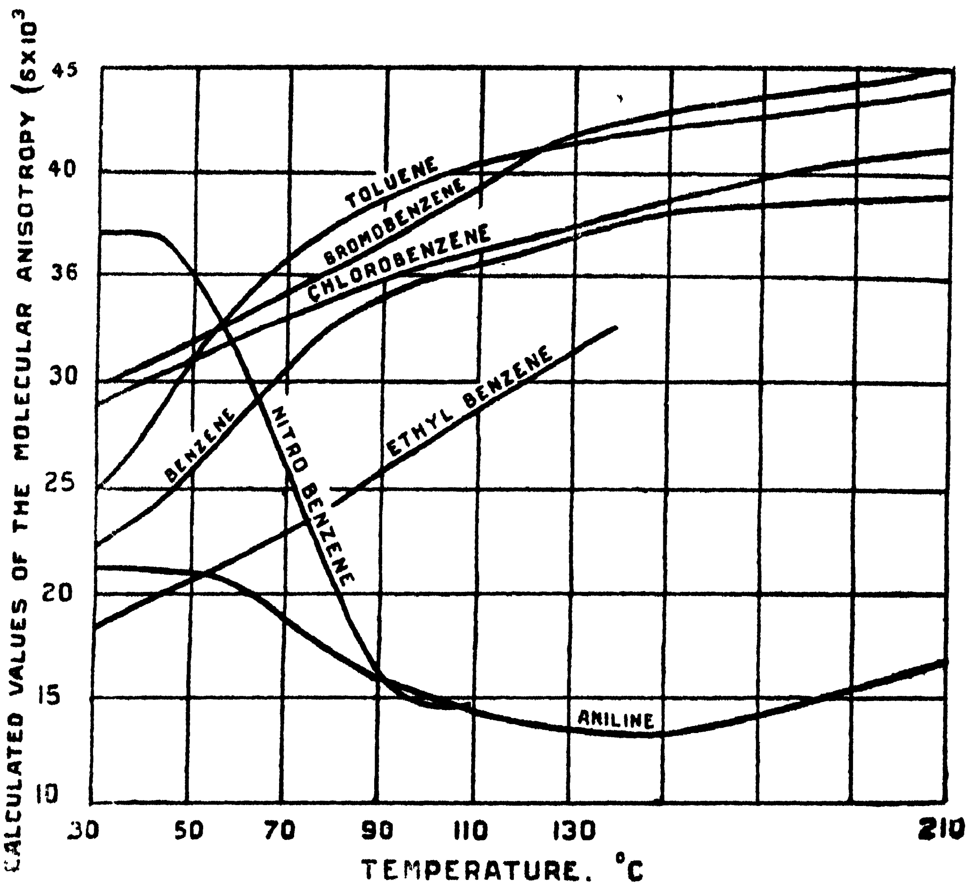

FIG. 22.

It is experimentally found that δ calculated for the molecules in the liquid state from eq. (xi) is usually different from δ for the same molecules in the vapour state calculated from (xii), the difference being due to the inter-molecular influences in the closely packed liquid state. When a liquid is heated $\delta_{liq.}$ would change and ultimately reach the δ_{gas} value when it is vapourised. Without again going just now in the cause of these variations, let us compare the temperature variations in $\delta_{liq.}$ for different liquids with our curves. The temperature variation of δ has been studied by Ramachandra Rao[14] for seven of the eight liquids used in the present investigation, *viz.*, benzene, toluene, ethylbenzene, chloro- and bromo-benzene, nitrobenzene and aniline. His curves are reproduced here (Fig. 22). While discussing the data about light scattering in fluids, Krishnan[15] has given values for $\delta_{\text{liq.}}$ for carbon disulphide at different temperatures taken from unpublished results of Ramanathan. Of the two series of value given by him based on two different formulæ used in the calculations, the values from the one that has been accepted

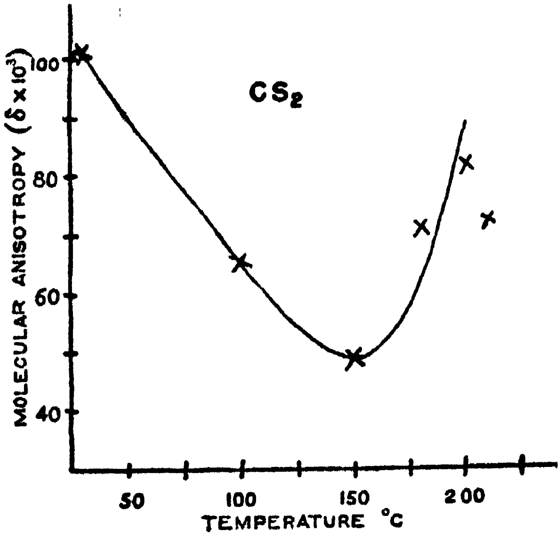

FIG. 23.

at present (eq. xi) are taken, and Fig. 23 represents the curve drawn from those values. The values of $\delta_{\text{liq.}}$ when the temperature is further increased will asymptotically tend to reach the value for $\delta_{\text{vap.}}$; and hence comparison of $\delta_{\text{liq.}}$ and $\delta_{\text{vap.}}$ for these substances should be taken note of in conjunction with the above curves. In Table 22 are given the values of $\delta_{\text{liq.}}$ and $\delta_{\text{vap.}}$ for the eight liquids used, after I. Ramakrishna Rao.[16]

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[14] S. Ramachandra Rao, Ind. Jour. Phys., *3*, 21 (1928).

[15] K. S. Krishnan, Proc. Ind. Assn. Cult. Sc., *9*, 268 (1926).

I. Ramakrishna Rao, Ind. Jour. Phys., *2*, 61 (1927).

TABLE 22.

Substance.	Benzene.	Toluene.	Ethyl benzene.	Chloro-benzene.	Bromo-benzene.	Aniline.	Nitro-benzene.	CS_2.
δ liq. $\times 10^3$	22	22	21·9	27	31	21·7	53	106
δ vap. $\times 10^3$	39·1	43·7	41·5	43·9	46·9	54·7	50	106

It is interesting to find that only in the two cases of nitrobenzene and carbon disulphide for which the birefringence concentration curves are convex towards the axis of concentration do we find the optical anisotropy of molecules in the liquid and vapour states to be practically the same. Again for these two liquids only is $\delta_{\text{lid.}}$ found at first to diminish to a great extent with the increase of temperature, and then to begin to increase. Even at temperatures much higher than those reached in Figs. 22 and 23, the value of $\delta_{\text{liq.}}$ would only tend to approach the $\delta_{\text{vap.}}$ value, being actually always less than it. Since $\delta_{\text{liq.}}$ is nearly the same as $\delta_{\text{vap.}}$ for these two, it is seen that with the increase of temperature, the optical anisotropy $\delta_{\text{liq.}}$ of the molecules will always be less than that at room temperature. A similar diminution of the effective optical anisotropy with dilution would give for nitrobenzene and carbon disulphide curves like the experimental ones.

For the other liquids for which the birefringence curves are concave towards the concentration axis or nearly straight, $\delta_{\text{liq.}}$ is found to increase with temperature. Apparently for the case of aniline, the temperature variation curve shows a slight and gradual diminution up to about 140° after which however $\delta_{\text{liq.}}$ has begun to increase, but on looking at its $\delta_{\text{vap.}}$ value which is much higher than $\delta_{\text{liq.}}$ one can see that for further increase of temperature, $\delta_{\text{liq.}}$ will increase rapidly and become more than that at room temperature.

The curve for aniline in Figure 22 is only an initial part and not fully representative. In fact, the difference between $\delta_{\text{vap.}}$ and $\delta_{\text{liq.}}$ for aniline is much greater than that for any of the other seven liquids, for many of which $\delta_{\text{liq.}}$ increases rapidly with temperature. Thus, the temperature—$\delta_{\text{liq.}}$ curve for aniline taken together with the difference in $\delta_{\text{vap.}}$ and $\delta_{\text{liq.}}$ values is fully consistent with the nature of its birefringence-concentration curve which is concave towards the concentration axis, according to the arguments developed above.

On comparing the $\delta_{\text{liq.}}$-temperature and the birefringence-concentration curves a striking similarity is again found in the variations of the general slopes of the former curves and the variations in the curvatures of the latter curves as we pass from benzene, through toluene, ethyl benzene, bromo-benzene and chlorobenzene to nitrobenzene. The rate of increase of $\delta_{\text{liq.}}$ with temperature decreases after benzene and toluene and ultimately becomes negative in nitrobenzene; this corresponds to the curvature of the birefringence curve of benzene which becomes less for toluene, ethyl benzene and bromo- and chloro-benzene and ultimately reverses for nitrobenzene. In benzene, the magnetic birefringence in a diluted state has a value higher than that indicated by theory and this corresponds to the higher values of $\delta_{\text{liq.}}$ for benzene molecules with increase of temperature. For nitrobenzene, the opposite is the case both for $\delta_{\text{liq.}}$ as well as for birefringence. In these comparisons again, as in the previous ones for temperature variation of birefringence, we do not expect a strict quantitative correspondence for each case.

9. *Conclusion from the Preceding Discussions.*

The different comparisons made so far are of experimental facts and do not rest on any particular theory about these variations. A more direct comparison would be with change of optical anisotropy with dilution, but data about it are wanting at present. But the comparisons made and the striking similarities seen in the preceding paragraphs between birefringence in mixtures and data about three different phenomena, *viz.*, (1) temperature variation of magnetic birefringence, (2) temperature variation of the optical anisotropy of molecules and (3) the optical anisotropy of molecules in the liquid and gaseous states, seems definitely to indicate that the variation in the optical anisotropy is at least one, and probably the main, cause of the deviations of the values of magnetic birefringence of liquid mixtures from those to be expected theoretically.

10. *Remarks on the Physical Interpretation.*

When one tries to picture the mechanism of these variations, different factors have to be considered. In polar molecules, dipolar association plays an important part. It is well known that dilution breaks up the molecular association, and this breaking up of association will in general change the observed molecular anisotropy. Some peculiarities in his investigations have been attributed to molecular association by Ramachandra Rao. In our mixtures, the asymmetry of the aniline curves seems to be due to association, aniline being strongly polar. Probably the aniline molecules in the unassociated state have a higher effective magneto-optic anisotropy than in the associated state. When the liquid is diluted, in the initial stages the diminution of birefringence due to the diminution in the number of molecules is compensated for by the breaking up of association and the consequent increase in molecular anisotropy, and so in these stages, the rate of diminution of birefringence with dilution is small. Afterwards, when a large number of molecules have been broken up, the diminution due to dilution preponderates, and the rate of decrease of birefringence becomes large.

In non-polar substances also it is known that close packing as in liquids changes the molecular anisotropy, it being generally different from that in the vapour state. Raman and Krishnan[10] have shown that this can be explained as due to the non-symmetrical distribution of molecules round a given one, producing an anisotropy in the polarisation field at the given molecule due to the surrounding ones. This anisotropic polarisation field depends upon the non-symmetrical shape of the molecule and the closeness of approach of the surrounding molecules to it. In general, the effect is to diminish the molecular optical anisotropy. With increasing temperature, the molecules get more space for themselves and the distribution of molecules round a given one becomes more symmetrical, and the optical anisotropy increases. The temperature variation curves of the non-polar hydrocarbons have been shown to agree with those to be expected on the above ideas of the anisotropic polarisation field.[17] The temperature variation and dilution, however, stand on a different footing so far as the above theory of anisotropic polarisation field is concerned. When the temperature is increased, due to the greater free space available the region of approach of the surrounding molecules to a given one become more nearly symmetrical, and the anisotropy of the polarisation field diminishes. But the effect of dilution is simply to replace the molecules surrounding a given one from its own kind to that of the diluent; but the distribution of the molecules of the second liquid and the consequent polarisation field will still remain unsymmetrical, this being dependent only on the shape of the given molecule. If, however, we assume that the diminution in the optical anisotropy is due not merely to the unsymmetrical distribution round a given one, but also to some kind of temporary molecular grouping in the liquid state, then the breaking up of this temporary grouping both due to an increase of temperature and due to dilution would explain the general correspondence between the two phenomena observed above. Such temporary grouping has also been suggested from X-ray diffraction in liquids and other observations.[18] Experimental study of variation of optical anisotropy in mixtures would also throw light on the points raised here.

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[17] Krishnan and Ramachandra Rao, Ind. Jour. Phys., 4, 39 (1929).

In conclusion, the author desires to express his heartfelt thanks to Professor Sir C. V. Raman, Kt., F.R.S., N.L., for his keen interest and kind encouragement. Thanks are also due to the King Edward Memorial Society, Nagpur, for having extended the term of the Research Scholarship.

e.g., Stewart, Phys. Rev., *32*, 558 (1928). K. Banerjee, Ind. Jour. Phys., *4*, 541 (1930).

TABLES.

v_1.	Shift.	Relative Birefringence.	v_1.	Shift.	Relative Birefringence.
	1 Benzene-CCl_4			4 Toluene-CCl_4	
0	0	0	0	0	0
0·176	21·0	0·251	0·177	14·5	0·204
0·378	38·5	0·461	0·372	28·5	0·401
0·583	53·5	0·641	0·606	43·0	0·606
0·850	73·0	0·874	0·787	57·0	0·803
1	83·5	1	1	71·0	1
	2 Benzene-Cyclohexane			5 Toluene-Cyclohexane	
0	insensible	...	0	insensible	...
0·215	19·0	0·306	0·265	21·5	0·307
0·395	32·5	0·529	0·523	42·0	0·600
0·541	39·0	0·634	0·708	55·5	0·793
0·712	50·0	0·813	0·805	60·0	0·857
1	61·5	1	1	70·0	1
	3 Benzene-Acetone			6 Ethyl benzene-CCl_4	
0	6·0	0·080	0	0	0
0·237	29·0	0·387	0·332	27·0	0·329
0·357	38·0	0·507	0·427	34·0	0·415
0·588	53·0	0·707	0·639	52·0	0·634
0·737	61·5	0·820	0·819	68·0	0·829
1	75·0	1	1	82·0	1

TABLES (*contd.*).

v_1.	Shift.	Relative Birefringence.	v_1.	Shift.	Relative Birefringence.
7 Ethyl benzene-Cyclohexane			10 Chlorobenzene-Acetone		
0	insensible	...	0	6·5	0·063
0·205	18·0	0·234	0·145	19·5	0·187
0·410	36·0	0·468	0·210	24·5	0·234
0·543	47·5	0·617	0·462	46·0	0·448
0·712	56·0	0·727	0·750	69·5	0·678
0·800	63·5	0·825	1	97·5	1
1	77·0	1			
8 Chlorobenzene-CCl_4			11 Bromobenzene-CCl_4		
0	0	0	0	0	0
0·313	28·0	0·326	0·198	20·0	0·203
0·496	42·5	0·494	0·397	36·5	0·370
0·581	49·5	0·576	0·626	65·0	0·660
0·738	65·5	0·762	0·788	76·5	0·777
1	86·0	1	1	98·5	1
9 Chlorobenzene-Cyclohexane			12 Bromobenzene-Cyclohexane *		
0	insensible	...	0	8·0	0·080
0·287	28·0	0·331	0·260	33·5	0·337
0·466	40·0	0·473	0·356	40·5	0·407
0·608	52·0	0·615	0·485	51·5	0·518
0·747	63·5	0·752	0·690	74·5	0·749
1	84·5	1	1	99·5	1

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* The sample of cyclohexane used for these two mixtures had an appreciable benzene impurity.

TABLES (*contd.*)

v_1.	Shift.	Relative Birefringence.	v_1.	Shift.	Relative Birefringence.
13 Nitrobenzene-CCl_4			16 Aniline-CCl_4		
0	0	0	0	0	0
0·342	14·0	0·207	0·197	20·0	0·274
0·526	25·5	0·378	0·418	38·5	0·528
0·717	37·0	0·548	0·592	53·0	0·726
0·778	40·0	0·593	0·761	65·0	0·890
1	67·5	1	1	73·0	1
14 Nitrobenzene-Cyclohexane			17 Aniline-Cyclohexane*		
0	insensible		0	8·0	0·112
0·211	12·0	0·189	0·358	39·0	0·549
0·400	21·5	0·339	0·490	49·0	0·690
0·554	31·0	0·488	0·652	59·5	0·838
0·736	41·0	0·646	0·793	68·0	0·957
1	63·5	1	0·912	69·5	0·979
			1	71·0	1
15 Nitrobenzene-Chlorobenzene			18 Aniline-Acetone		
0	28·5	0·305	0	9·0	0·126
0·318	41·0	0·439	0·251	30·0	0·420
0·422	45·5	0·487	0·390	45·5	0·636
0·615	59·5	0·637	0·615	62·0	0·867
0·768	70·0	0·749	0·851	66·5	0·930
1	93·5	1	1	71·5	1

TABLES (*contd.*)

v_1.	Shift.	Relative Birefringence.	v_1.	Shift.	Relative Birefringence.
	19 CS_2-CCl_4			20 CS_2-Cyclohexane	
0	0	0	0	insensible	
0·265	10·5	0·216	0·140	5·0	0·101
0·392	14·5	0·299	0·318	12·5	0·253
0 578	25·0	0·515	0·496	19·0	0·384
0 708	32·0	0·659	0·673	28·0	0·566
1	48·5	1	1	49·5	1

v_1.	Shift.	Relative Birefringence.
	21 CS_2—Benzene	
0	−58·5	−1·31
0·239	−36·0	−0·81
0·428	−17·0	−0·38
0·615	4·0	0·09
0·795	19·5	0·44
1	44·5	1

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Raman Spectra of Iodides : Part II. Ethyl, Propyl and Isobutyl Iodides.

By

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(Plate XXXI.)

(Received for publication, 16th November, 1932.)

Abstract.

The results of a study of the Raman spectra of ethyl, propyl and isobutyl iodides are described in this paper. In order to prevent the liquid getting coloured due to photochemical decomposition continuous distillation is maintained during the exposure. Besides, the free iodine which is not removed by this means is removed completely by means of copper wire placed suitably in the path of the distillate. Isobutyl iodide is studied for the first time. In all cases several new frequencies have been obtained. The following Raman frequencies are reported:

Ethyl iodide: 262 (6) ; 502 (9) ; 952 (2) ; 1049 (0) ; 1203 (3) ; 1380 (0) ; 1438 (1) ; 2860 (1) ; 2915 (4) ; 2968 (3) and 3016 (2).

Propyl iodide: 133 (0), 204 (2) ; 291 (3) ; 390 (2) ; 504 (6) ; 592 (4) ; 758 (1) ; 809 (1); 873 (1) ; 1012 (2) ; 1120 (3) ; 1191 (2) ; 1267 (0) ; 1325 (0) ; 1385 (0) ; 1424 (1) ; 1442 (1) ; 1487 (0) ; 2836 (2) ; 2882 (1) ; 2929 (3) ; 2959 (2) and 3035 (0). Nine frequencies are reported for the first time.

Iso-butyl iodide: 173 (1) ; 285 (3) ; 430 (3) ; 580 (2*b*) ; 605 (3) ; 792 (1) ; 943 (0 *b*) ; 1194 (3) ; 1304 (1) ; 1477 (0) ; 2860 (2) ; 2960 (2); 3001 (1).

1. *Introduction.*

In a previous paper,[1] the author investigated the Raman spectra of methyl-iodide and phosphonium iodide. Three other iodides, *viz.*, ethyl, propyl and isobutyl iodides are examined and the results are reported here. As we ascend the series: methyl, ethyl, propyl, butyl, etc., the iodides show greater and greater tendency for photochemical decomposition.

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[1] Ind. Jour. Phys., 7, 285 (1932).

Consequently, the liquids get highly coloured under the influence of light with the formation of free iodine. This is a serious difficulty which stands in the way of getting good spectrograms. A modification of the constant distillation apparatus was devised to overcome this difficulty and is described below.

2. *Experimental Details.*

The liquids as supplied by Kahlbaum in coloured capsules are colourless but acquire a deep colour on exposure to light. The coloured liquid is first shaken with a dilute solution of sodium bisulphite which removes most of the free iodine. The liquid still has a yellowish tint and to get it perfectly colourless it is dehydrated with calcium chloride and then left in contact with bright copper wire for some time. Any free iodine which is present is thus removed as copper iodide which gets deposited on the metal as a dull brownish red film. After this preliminary purification, the liquid is distilled in vacuum and the middle fraction is transferred to the apparatus shown in Fig. 1. *A* is a distilling flask with a side tube *B* which is surrounded by a water jacket *C*. In the U-tube *D* freshly reduced copper in the form of fine wire is closely packed. The U-tube is sealed on to be observation tube *E* on the one side and to the side tube *B* on the other. The liquid from *D* enters

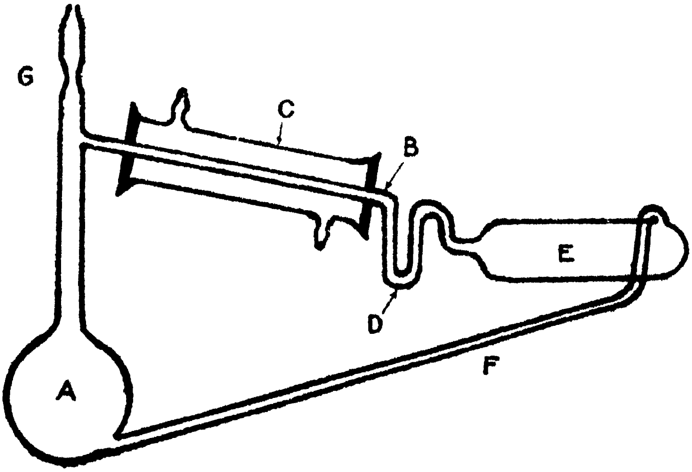

FIG. 1.

the observation tube which is illuminated by the light from the mercury arc focussed on to it by a condenser. After the tube *E* is filled, the distillate overflows into the tube *F* and is finally carried back to the flask *A*. The cycle continues: fresh liquid entering on one side and the spent liquid overflowing from the other. After pouring the liquid into the flask *A*, the apparatus is connected to a pump, evacuated and is sealed off at *G*. The rate of distillation is so adjusted that the liquid remains in contact with copper for a fairly long time and when it overflows into the observation tube *E*, it is colourless. The efficiency of interposing the U-tube packed with copper wire becomes evident when it is noted that in its absence the liquid accumulating in the observation tube acquires a red colour inspite of the continuous distillation. With the arrangement described the liquid was perfectly colourless even after 4 days' exposure to the mercury lamp.

A simple method of placing a long copper wire inside the observation tube was attempted but was not found to be very efficient. In order to completely decolourise the liquid, it is necessary to increase the surface of the copper exposed. This, however, interferes with the illumination of the liquid and is not practicable. Further, in course of time, fine particles of copper iodide get detached from the wire and remain suspended in the liquid thereby causing strong continuous spectrum. In the arrangement described, these difficulties do not arise. The copper wire at the top of the left limb of the U-tube decolourises the liquid and any powder which gets detached is retained by the long column of closely packed wire. The spectrogram obtained after exposing the liquid for 96 hours is absolutely free from any continuous background.

The usual experimental arrangements were adopted, using a mercury lamp as the source of incident light. The spectrum of the scattered light was photographed with a large dispersion Fuess instrument using backed Ilford Golden Iso-zenith plates. The wave-lengths were calculated on the micrometer measurements using Hartmann's simplified interpolation formula taking the incident mercury lines as the standards.

3. *Results.*

The following tables give the analysis of the Raman spectra of the three liquids studied here. The intensities (I), wave number (ν) and the shifts in the frequencies ($\Delta\nu$) of the Raman lines are shown under the respective columns. The incident mercury lines at λ 4046·6, 4077·8, 4339·2, 4347·5 and 4358·3 are represented by the letters *d*, *e*, *f*,

TABLE I: Ethyl Iodide.

I	ν	$\Delta\nu$	I	ν	$\Delta\nu$
1	24257	*e*—259	9	22436	*f*—502
7	24204	*d*—501	2	21986	*f*—952
2	24014	*e*—502	0	21887	*f*—1051
2	23754	*d*—951	1	21847	*d*—2858
0	23658	*d*—1047	4	21789	*d*—2916
3	23502	*d*—1203	6*b*	21735	*d*—2970
3	23438	*f*+500			*f*—1203
0	23324	*d*—1381	0	21689	*d*—3016
1	23266	*d*—1439	0	21599	*e*—2917
3	23199	*f*+261	1	21559	*f*—1379
0	22778	*h*—261	2	21501	*e*—3015
0	22732	*g*—263			*f*—1437
6	22677	*f*—261	0	20076	*f*—2862
0	22538	*h*—501	2	20028	*f*—2910
0	22492	*g*—503	2	19972	*f*—2966

Author $\Delta\nu$	262	501	951	1049	1203	1380	1438	2860	2916	2968	3016
	(6)	(9)	(2)	(0)	(3)	(0)	(1)	(1)	(4)	(3)	(2)
Dadieu and Kohlrausch.	261	497	951	1049	1194		1430	2858	2916	2967	3012
Infra-red frequency.			952	1041	1196	1389	1408				

TABLE II : Propyl Iodide.

I	ν	Δν	I	ν	Δ	I	ν	Δν
0	24413	d—292	0	22805	f—133	4	21747	d—2958
1	24200	d—505	2	22734	f—204			f—1191
1	24113	d—592	3	22648	f—290	0	21685	e—2831
0	23948	d—757	2	22548	f—390	0	21671	d—3034
0	23898	d—807	6	22434	f—504			f—1267
0	23695	d—1010	4	22347	f—591	0	21616	f—1322
0	23583	d—1122	1	22180	f—758	0	21553	-187
1	23513	d—1192	1	22127	f—811	1	21513	f—1425
0	23437	d—1268	1	22065	f—873	1	21494	f—1444
0	23377	d—1328	2	21923	f—1015	0	21452	f—1486
0	23320	d—1385	2	21862	d—2843	1	20104	f—2834
0	23283	d—1422	3br	21820	d—2885	1	20059	f—2879
0	23265	d—1440			f—1118	1	20010	f—2928
0	23217	d—1488	3	21776	d—2929	1	19978	f—2960
0	23143	f+205				0	19903	f—3035

Author Δν =	133	204	291	390	504	592	758	809	873	1012	1120	1191	1267	1325	1385	1424	1442	1487	2836	2882	2929	2959	3035
	(0)	*(2)	(3)	(2)	(5)	(4)	(1)	(1)	(1)	(2)	(1)	(2)	(0)	(0)	(0)	(1)	(1)	(0)	(1)	(1)	(3)	(2)	(0)
Dadieu—Kohlrausch Δν =	...	198	285	389	503	590	760	817	877	1017	...	1184	1272	...	...	1427	...	...	...	...	2935	...	...

* The figures in the bracket show the relative intensities of the lines.

TABLE III : Isobutyl Iodide.

I	ν	$\Delta\nu$	I	ν	$\Delta\nu$
0	24421	$d-281$	3	22653	$f-285$
1	24274	$d-431$	3	22509	$f-429$
1	24123	$d-582$	2*b*	22361	$f-577$
3	24100	$d-605$	3	22333	$f-605$
2	23912	$d-793$	1	22146	$f-792$
		$e-604$	0*b*	21995	$f-943$
0	23761	$d-944$	1	21844	$d-2861$
3	23514	$d-1191$	1	21800	$g-1195$
		$f+576$	3	21744	$f-1194$
½	23399	$d-1306$			$d-2961$
0	23368	$f+430$	1	21704	$d-3001$
1*b*	23229	$f+291$	1	21684	$f-1304$
		$d-1476$	0	21461	$f-1477$
1	23110	$f+172$	1	20079	$f-2859$
1	22764	$f-174$	1	19979	$f-2959$

$\Delta\nu$ = 173 (1) ; 285 (3) ; 420 (3) ; 580 (2*b*) ; 605 (3) , 792 (1) ; 943 (0*b*) ; 1194 (3) ; 1304 (1) ; 1477 (0) ; 2860 (2) ; 2960 (2) ; 3001 (1).

g and *h* respectively. The values obtained by other investigators are given for comparison. Infra-red absorption data are available only in the case of ethyl iodide and are taken from Coblentz's 'Investigations of Infra-red spectra.' Only those values which correspond to the Raman frequencies are included in the table.

4. *Discussion of Results.*

The Raman spectrum of ethyl iodide has been investigated by Dadieu and Kohlrausch[2] and it is seen from the table that there is good agreement between their results and those obtained by the author. A new line at $\Delta\nu$ 1380 which was not reported before has been obtained. The line is weak in intensity and fairly sharp in character. The spectrum of propyl iodide has also been studied by the above authors, but several Raman frequencies characteristic of this liquid have been overlooked by them. As many as nine new frequencies are recorded for the first time by the author. These are at $\Delta\nu$ 1120, 1325, 1385, 1442, 1487, 2836, 2882, 2959 and 3035. The CH band at 2935 reported by Dadieu and Kohlrausch has been resolved into five components ranging from 2836 to 3035.

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[2] Wien Ber., *139*, 77 (1930).
" " *139*, 717 (1930).

It has been shown previously that all the iodo compounds show a prominent Raman frequency at about $\Delta\nu$ 500, which may be attributed to the oscillation of the C-I group. It is of interest to study the variation in magnitude and intensity of this frequency in the various iodo compounds. In methyl iodide this frequency appears with great intensity ($\Delta\nu$ 524) and the corresponding Raman line shows rotational wings on either side. In ethyl iodide the line is quite prominent but shows a distinct shift towards the shorter wavelength. In the higher members the line continues to appear at about the same position as in ethyl iodide. A similar diminution occurs in the values of the frequencies characteristic of the CBr and CCl linkages respectively from the first to the second members of the series. The respective frequencies attain a more or less steady value in the propyl and the higher members as is seen from the table given below.

TABLE IV.

	Cl.	Br.	I.
Methyl	712	594	524
Ethyl	655	557	502
Propyl	651	565	504
Butyl	650	557	505

In this connection it may be noted that a similar observation with the CS oscillation [3] in the mercaptans and organic sulphides has been made.

On examining the spectrum of isobutyl iodide it is observed that the frequency characteristic of the CI oscillation which

TABLE V.

Ethane.		Ethyl Chloride.		Ethyl Bromide.		Ethyl Iodide.	
Infra-red.	Scattering.	Infra-red (Liq.).	Scattering.	Infra-red (Liq.).	Scattering.	Infra-red (Liq.).	Scattering.
...	...	...	...	...	148 (1)	...	...
...	...	...	337 (5)	...	290 (3)	...	261 (6)
...	..	...	438 (½)	...		...	...
..	...	...	655(10)	...	557 ( )	...	502 (9)
...	...	...	...	...	...	667	...
...	...	...	...	...	...	709	...
757	...	...	...	...	..	735	...
800	...	...	...	...	...	826	...
819	...	No	...	No	...	856	...
837	...	Data.	...	Data.	...	893	...
...	993 (3)	...	966 (4)	...	...	952	951 (2)
...	...	...	1071 (3)	...	1063 (1b)	1041	1049 (0)
...	...	...	1276 (½b)	...	1240 (1b)	1196	1208 (3)
...	...	...	...	...	...	1389	1380 (0)
1459	1460 (1)	...	1448 (4)	...	1439 (2b)	1408	1438 (1)
...	...	...	...	...	...	1695	...
...	...	...	...	...	...	1894	...
...	...	...	...	...	...	2173	...
...	2900 (5)	...	2875 (4b)	...	2869 (2)	...	2860 (1)
2949	2955 (5)	...	2930 (8b)	...	2924 (4)	2983	2915 (4)
...	...	...	2966 (8)	...	2964 (2)	...	2968 (3)
...	...	...	...	...	...	...	3022 (2)

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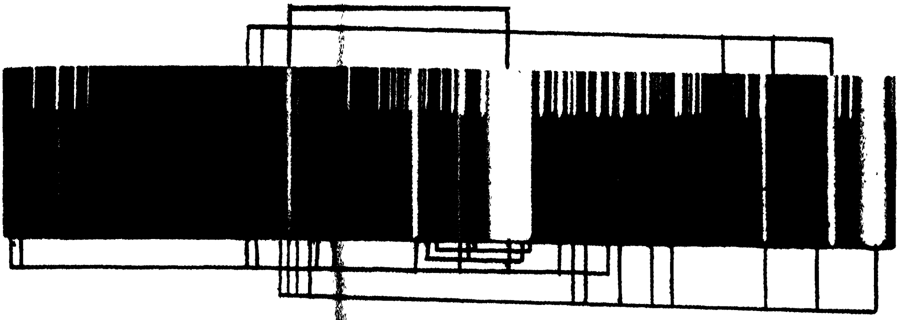
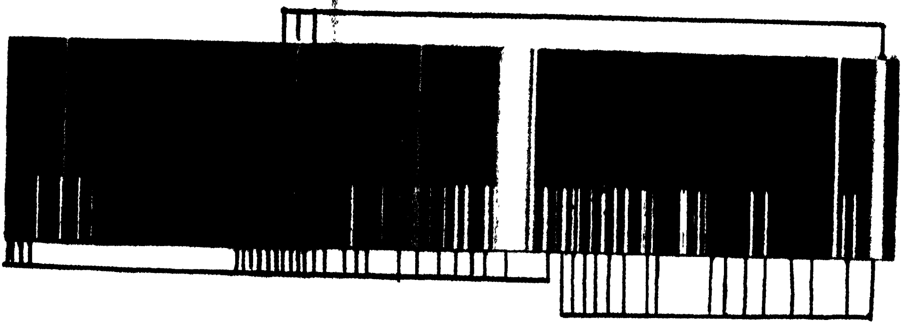
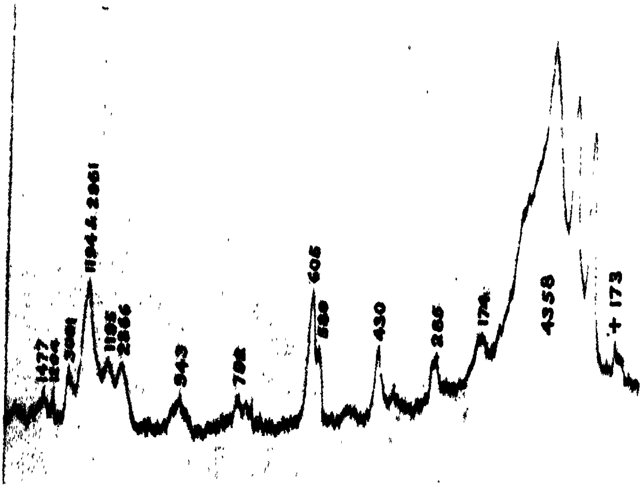
[3] S. Venkateswaran, Ind. Jour. Phys., 5, 219 (1930).







(a) Ethyl iodide.

(b) Propyl iodide.

(c) Iso butyl iodide.

TABLE VI.

Propane.	Propyl Chloride.	Propyl Bromide.	Propyl Iodide.
...	...	...	133 (0)
...	...	...	204 (2)
337 (2)	335 (4)	315 (3)	291 (3)
...	418 (2)	403 (2b)	390 (2)
...	...	565 (6)	594 (6)
...	651 (5)	648 (4)	592 (4)
...	725 (4)	...	...
...	789 (3)	777 (2)	758 (1)
867 (10)	850 (2)	840 (1)	809 (1)
...	892 (2)	892 (1b)	873 (1)
1055 (2b)	1028 (3)	1028 (2b)	1012 (2)
1155 (2)	1105 (0)	...	1120 (3)
...	...	...	1191 (2)
...	1289 (0)	...	1267 (0)
...	1339 (1)	...	1325 (0)
...	...	...	1385 (0)
1453 (4)	1446 (4b)	1434 (2)	1424 (1)
...	...	...	1442 (1)
...	...	...	1487 (0)
2728 (3)	...	...	2836 (2)
2757 (1)	...	...	...
2874 (10)	2878 (5)	2875 (1b)	2882 (1)
2903 (3)	...	...	...
2920 (5)	2935 (7)	2935 (4)	2929 (3)
2945 (3)	2957 (7)	2960 (5b)	2959 (2)
...	2975 (0)	...	...
2968 (3)	2998 (0)	2998 (2b)	...
...	3019 (0)	...	3035 (0)

appears strongly in all the normal compounds could not be detected on the plate. This weakening in the intensity of the Raman line, characteristic of any group in the iso compounds, appears to be of a general nature. For instance, Bhagavantam and Venkateswaran[4] noticed a diminution in the CCl and CO lines in the isopropyl chloride and trimethyl carbinol respectively.

The 3 μ band due to hydrogen generally appears with a large number of components in the case of the higher members of the series. A striking feature has been noticed by Venkateswaran[5] which differentiates the normal and iso derivatives. In the case of the normal derivatives the component at the centre of the band is most intense, while in the case of the iso derivatives the outer components are more intense. This is seen to hold good in the case of normal and iso iodides also. The lines at about 1450 are usually attributed to the transverse oscillation of the hydrogen atoms.

Another interesting comparison to be pointed out at this stage is the one that arises out of the series :—

C_2H_6; C_2H_5Cl; C_2H_5Br; C_2H_5I...... (*vide* Table V).

and C_3H_8; C_3H_7Cl; C_3H_7Br; C_3H_7I...... (*vide* Table VI).

which illustrates the influence of substituting one of the hydrogen atoms in the parent hydrocarbon by one halogen atom. There is a diminution in the value of the characteristic frequency of the carbon-halogen system as the mass of the halogen is increased. Thus $\Delta\nu 655$ in the case of the chloro derivative falls to $\Delta\nu 502$ in the iodo compound. The $\Delta\nu 993$ in the ethane has been attributed to the $C-C$ oscillation and as the molecule is loaded more and more heavily by substituting one of the hydrogen atoms by chlorine, or bromine or iodine atom respectively, the frequency diminishes to $\Delta\nu 966$, and finally to 951. In the case of the bromide, this line is missing. The carbon-hydrogen frequencies do not show such a large diminution, though they shift as the mass of substituent is increased. Thus both the 2900 and 2955 lines in ethane diminish by 25cm.$^{-1}$ when hydrogen is replaced by one chlorine atom. By the introduction of a bromine atom, the lines shift to 2869 and 2924 respectively, *i.e.*, by 31 wave numbers. Finally when the iodine atom is introduced, both of them diminish again by 40 wave numbers. It is interesting to observe that the 2966 frequency in ethyl chloride remains practically unchanged.

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[4] Proc. Roy. Soc., *127*, 360 (1930).

[5] Ind. Jour. Phys., *5*, 129 (1930).

The derivatives of propane also show most of the changes mentioned above. Only due to the complex nature of the molecule, the hydrogen frequencies do not show such a striking change as seen in the derivatives of ethane.

The author's grateful thanks are due to Sir C. V. Raman, F.R.S., who kindly suggested the problem and under whose kind guidance the work was carried out.

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The New Statistics and Electrostatics.

By

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(Received for publication, 16th November, 1932.)

ABSTRACT.

Silberstein's application of the theory of metallic conductors to electrostatics is reconsidered from the standpoint of the new statistics, distinguishing therein two important cases. It is found that linear integral equations of the second kind are arrived at similar to the one obtained by him, but with altered constants, and in one of the cases dicussed, an extra constant factor [a of eq^n (17)] appears in the integral equation. The thickness of the electrified layer in charged conductors is obtained equal to $2{\cdot}08 \times 10^{-8}$cm. and this is found to be independent of the temperature of the conductor.

L. Silberstein[1] in the year 1918 realised that the application of the theory of metallic conductors to problems in electrostatics may not be devoid of interest and importance from the theoretical point of view. But no attempt has till now been made to bring his equations in line with the remarkable recent developments in the theory of electron conduction due to Pauli, Sommerfeld[2] and others.

The problem to be attacked may be stated as follows: Given the total charge of each conductor and the potential ϕ_e of the external field, due to charges fixed outside the conducting masses, find the electrostatic or equilibrium distribution of electricity over each of the conductors. Silberstein in his treatment assumed the Maxwell-Boltzmann distribution law for the free electrons inside the conductors, whereas the development of the quantum statistics of degenerate systems shows that they ought to be governed by the Fermi-Dirac formula. Thus the number of free electrons per unit volume whose energy values between E and li E+dE, when in electrostatic-statistical equilibrium is given by

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[1] Phil. Mag., *36*, 413 (1928).

[2] Z. f. phys., *47*, 1 (1928).

$$dN = \frac{2\pi G}{h^3}(2m)^{\frac{3}{2}} \frac{E^{\frac{1}{2}}\, dE}{\frac{1}{A}\,\text{Exp.}\,\frac{E+\psi}{KT}+1} \tag{1}$$

ψ being an unknown function of x, y, z, is the potential energy of the electron in the resultant field of force. Since the electronic charge ϵ is to be regarded as a negative number

$$\psi = -\epsilon\,(\phi_e + \phi_i) = -\epsilon\phi \text{ (say)} \tag{2}$$

where ϕ_i is the potential of the (unknown) distribution of resultant charge within the conductors. Integrating (1) over the whole phase space we get the number of electrons per unit volume as

$$N = \frac{G}{h^3}\,(2\pi mKT)^{\frac{3}{2}}\, U_{\frac{1}{2}} \tag{3}$$

where $U_{\frac{1}{2}}$ is the particular case of the general Sommerfeld integral

$$U_\rho = \frac{1}{(\rho+1)} \int_0^{\infty} \frac{u^\rho\, du}{\frac{1}{B}e^u+1}$$

and

$$B = Ae^{-\frac{\psi}{KT}} \tag{4}$$

Equation (3) represents the non-degenerate or degenerate case for the electron system according as B <<1 or >>1. For intermediate values of B, the integral in (3) can only be evaluated graphically or by expanding in an infinite series[3] and as this leads to complication, we shall discuss only the cases of complete degeneracy or complete non-degeneracy. If the latter $U_\rho = B$ for all values of ρ and A in (4) is given by $A = \frac{nh^3}{G}(2\pi mKT)^{-\frac{3}{2}}$. Consequently equation (3) reduces to the classical expression arrived at by Silberstein, *viz.*,

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[3] Russel, S. Bartlett, P hy. Rev., 31, 959 (1931).

$$N = ne^{-\frac{\psi}{KT}} \tag{5}$$

whereas if $B >> 1$, and this condition does hold for the free electrons in metals, we have

$$U_\rho = \frac{u_0^{\rho+1}}{(\rho+2)}\left[1+2\left\{\frac{(\rho+1)\rho c_2}{u_0^2} + \frac{(\rho+1)\rho(\rho-1)(\rho-2)c_4}{u_0^4} + \ldots\ldots\right\}\right]$$

$$\text{and } u_0 = \log B, \quad A = \frac{h^2}{2mKT}\left(\frac{3n}{4\pi G}\right)^{\frac{2}{3}} \tag{6}$$

Evaluating (3) from these

$$N = \frac{G}{h^3}\,\frac{4}{3\sqrt{\pi}}\,(2\pi mkT)^{\frac{3}{2}}(\log B)^{\frac{3}{2}} \tag{7}$$

where terms of small value have been omitted. Here we must distinguish between two particular cases of importance :

$$\text{If } \left|\frac{\psi}{KT\log A}\right| < 1, \quad \text{from (4)}$$

$$(\log B)^{\frac{3}{2}} \;\underline{\Omega}\; (\log A)^{\frac{3}{2}}\left[1-\frac{3}{2}\,\frac{\psi}{KT\log A}\right]$$

and therefore, on simplification by using (6) and substituting in (7)

$$N = n - \gamma_2\psi \tag{8}$$

$$\text{where } \gamma_2 = \frac{4\pi G m}{h^2}\left(\frac{3n}{4\pi G}\right)^{\frac{1}{3}}$$

If $\left|\frac{\psi}{\text{KT} \log \text{A}}\right| > 1$, from (2) and (4)

$$(\log \text{B})^{\frac{3}{2}}\ \underline{\Omega}\left(\frac{\epsilon\phi}{\text{KT}}\right)^{\frac{3}{2}}\left[1 + \frac{3}{2}\,\frac{\text{KT} \log \text{A}}{\epsilon\phi}\right]$$

$$\text{and N} = \frac{4\pi G}{3h^3}(2m\epsilon\phi)^{\frac{3}{2}}\left[1 + \frac{3}{2}\,\frac{\text{KT} \log \text{A}}{\epsilon\phi}\right] \tag{9}$$

n is the number of free electrons per unit volume, of each conductor, in absence of the external field and, in the (microscopically) neutral or unelectrified state of the conductor. By the assumption of the theory n is also the number per unit volume of positively charged atoms, each carrying a charge ϵ. Thus the resultant density ρ of electric charge at the point x, y, z within any conductor of the system will be equal to $(n\epsilon - \text{N}\epsilon)$ where N is given by (5), (8) or (9) depending on the conditions of the problem under consideration.

Thus for the non-degenerate case, we naturally get Silberstein's equation

$$\rho = n\epsilon - n\epsilon\, e^{-\frac{\psi}{\text{KT}}} \tag{10}$$

whereas for the degenerate case

$$\text{if } \left|\frac{\psi}{\text{KT} \log \text{A}}\right| < 1, \quad \rho = \gamma_2 \epsilon \psi \tag{11}$$

$$\text{and if } \left|\frac{\psi}{\text{KT} \log \text{A}}\right| > 1 \quad \rho = n\epsilon - \frac{4\pi G}{3h^3}\epsilon^{\frac{5}{2}}(2m\phi)^{\frac{3}{2}}\left[1 + \frac{3}{2}\,\frac{\text{KT} \log \text{A}}{\epsilon\phi}\right]$$

Let us assume that $\frac{3}{2}\,\frac{\text{KT} \log \text{A}}{\epsilon\phi}$ is negligible compared to unity.

Then $$\rho = n\epsilon - \frac{4\pi G}{3h^3}\,\epsilon^{\frac{5}{2}}\,(2m\phi)^{\frac{3}{2}} \tag{12}$$

These equations, on further rearrangement of their terms give respectively

$$\left.\begin{aligned} \log\left(1-\frac{\rho}{n\epsilon}\right) &= \frac{\epsilon\phi}{KT} \\ \rho &= \gamma\,\epsilon^2\,\phi \\ (n\epsilon)^{\frac{2}{3}}\left(1-\frac{\rho}{n\epsilon}\right)^{\frac{2}{3}} &= \left(\frac{4\pi G}{3h^3}\right)^{\frac{2}{3}}\epsilon^{\frac{5}{3}}\,2m\phi \end{aligned}\right\} \tag{13}$$

If ρ' be the density in any element $d\,\tau'$ and r' the distance of $d\,\gamma'$ from the point x, y, z then taking the charges in rational units

$$\phi_i = \frac{1}{4\pi}\int\frac{\rho' d\gamma'}{r'}$$

integrated over the volume of all conductors of the system. Thus from this and (2), the equations (13) become

$$\begin{aligned} \log\left(1-\frac{\rho}{n\epsilon}\right) &= \frac{\epsilon\phi_e}{KT} + \frac{\epsilon}{4\pi KT}\int\frac{\rho' d\gamma'}{r'} \\ \frac{\rho}{\gamma_2\epsilon^2} &= -\phi_e - \frac{1}{4\pi}\int\frac{\rho' d\gamma'}{r'} \\ \left(\frac{3n}{4\pi G}\right)^{\frac{2}{3}}\frac{h^2}{2m\epsilon}\left(1-\frac{\rho}{n\epsilon}\right)^{\frac{2}{3}} &= \phi_e + \frac{1}{4\pi}\int\frac{\rho' d\gamma'}{r'} \end{aligned} \tag{14}$$

It has been assumed by leading electronists that $\frac{\rho}{n\epsilon}$ is a very small fraction, so that

$$\log\left(1-\frac{\rho}{n\epsilon}\right) \doteq -\frac{\rho}{n\epsilon}$$

$$\left(1-\frac{\rho}{n\epsilon}\right)^{\frac{2}{3}} \doteq 1-\frac{2}{3}\,\frac{\rho}{n\epsilon}$$

Thus, finally the equations (14) lead to the following linear integral equations of the second kind :—

$$\frac{\rho}{\gamma_1\epsilon^2} = -\phi_e - \frac{1}{4\pi}\int\frac{\rho' d\gamma'}{r'} \text{ (non-degenerate)} \qquad (15)$$

$$\text{where} \quad \gamma_1 = \frac{n}{\mathrm{KT}}$$

$$\frac{\rho}{\gamma_2\epsilon^2} = -\phi_e - \frac{1}{4\pi}\int\frac{\rho' d\gamma'}{r'} \left(\text{degenerate and } \frac{\epsilon\phi}{\mathrm{KT}\log \mathrm{A}} < 1\right) \qquad (16)$$

$$\text{and } \frac{\rho}{\gamma_3\epsilon^2} = \bar{a} - \phi e - \frac{1}{4\pi}\int\frac{\rho' d\gamma'}{r'} \left(\text{degenerate and } \frac{\epsilon\phi}{\mathrm{KT}\log \mathrm{A}} > 1\right) \qquad (17)$$

$$\text{where} \quad \gamma_3 = \gamma_2 \quad \text{and} \quad \bar{a} = \frac{h3^2}{2m\epsilon}\left(\frac{3n}{4\pi\mathrm{G}}\right)^{\frac{2}{3}}$$

These are the fundamental equations from which we will have to start for solving problems in electrostatic charge distribution on the basis of the electron theory.

2. It is seen by comparing equations (15), (16) and (17) that the constants involved in the equation for the classical case are altered by the application of the new statistics. Thus the penetration of the surface charge or the thickness of the electrified layer, which is measured by the square root of the coefficient of ρ in each of the equations (15), (16) and (17) is in the classical case given by

$$\frac{1}{\sqrt{\gamma_1\epsilon^2}} = \sqrt{\frac{\mathrm{KT}}{n\epsilon^2}}.$$

In the new statistics, however this becomes

$$\frac{1}{\sqrt{\gamma_1\epsilon^2}} = \frac{}{8\,(4^6\,\pi\,\mathrm{G})^{\frac{1}{3}}m^{\frac{1}{2}}\epsilon n^{\frac{1}{6}}}$$

$$= 2{\cdot}08 \times 10^{-8} \text{ cm},$$

we thus see that according to the Sommerfeld theory, the thickness of the electrical layer is independent of temperature. Moreover, it is also independent of the externally imposed eletric field as is evidenced by the equality of γ_2 to γ_3.

A similar result has been arrived at by Waterman[4] by modifying Thomson's[5] method of estimating the thickness and he gets it

$$\frac{h}{(4\cdot 3)^{\frac{1}{6}}\,\pi^{\frac{5}{6}}\,m^{\frac{1}{2}}\,\epsilon n^{\frac{1}{6}}}.$$

My best thanks are due to Sir C. V. Raman for his very kind encouragement.

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[4] Proc. Roy. Soc., *121*, 30 (1928).

[5] Thomson, Corpuscular Theory of Matter, p. 82.

The Vibrations of the Different Parts of the Pianoforte Sound-Board.

By

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(*Received for publication, 20th October, 1932.*)

ABSTRACT.

The vibrations of different parts of the pianoforte sound-board have been studied by a method described by the author in an earlier paper. It is found that the prominent harmonics present in the vibration curves of any one point persist in the curves for other points lying at various places on the sound-board. It is concluded that the entire sound-board vibrates as a whole inasmuch as the vibrations of all the ribs constituting the board are exactly similar in nature. It is, however, noted that the amplitudes of the various harmonics vary from rib to rib ; ribs of larger length produce higher harmonics of prominent amplitude whereas in the smaller ribs the higher harmonics disappear.

1. *Introduction.*

Welker[1] considers the strings to be of secondary importance while the sound-board plays the principal part in the formation of the tone. On the other hand the pianoforte makers[2] are of the opinion that the sounding-board is not at all tone producing but like the stretched membrane of the drum, is a sound producing body, and therefore only sound and not tone can be drawn from it. Whatever view may be taken, the sound-board plays a fundamental part in the production of the musical tones of the pianoforte. Its present shape and structure, have heen decided upon by trial and experience.

[1] " Der Clavierbaw in Senior Theorie, Technik and Geschichte," by H. Welker.

[2] " The Pianoforte and its Acoustic Properties," by Siegfried Hansing.

But very little has been done on the theory of the sound-board vibrations.

In 1910, G. H. Berry[3] in the course of his investigations on the pianoforte sound-board remarked that different sections of the sound-board have different lengths and thicknesses and hence have different frequencies. He also took some photographs of the vibrations of the sound-board at different places and found them different in shape. But he did not study the vibrations of the sound-board as a whole. Subsequently Sir C. V. Raman[4] devised a method for obtaining the vibration curves of the sound-board with the instrument as actually played upon, and set out certain general conclusions regarding the theory of the sound-board. In 1929, the author also photographed the vibrations of the pianoforte sound-board, in the laboratory of the Indian Association for the Cultivation of Science, Calcutta, and derived a certain number of conclusions from the analysis of the vibration curves. The details of the method used, and the conclusions drawn were published in a previous paper[5] by the author.

In the present paper, the author has studied the vibrations of different parts of the pianoforte sound-board, in order to know whether the entire board vibrates with one frequency as a whole, or its different parts (as the sound-board consists of different pieces of wood joined together by means of ribs which are attached at some inclination with the vertical plane of the board) vibrate with different frequencies, and whether maxima which are prominently present in the vibration of one part persist in the case of the vibrations of the other parts as well. Certain improvements effected in the method are also described below. The present work throws much light on the investigations of D. C. Miller[6] and others.

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[3] Phil. Mag., *20*, 652 (1910) and Nature, *85*, 541 (1911).

[4] Handbuch der Phys., 8, 354 (1927).

[5] Ind. Jour. Phys., *4*. 515 (1930).

[6] "The Science of Musical Sounds," by D. C. Miller.

2. *Experimental Arrangement.*

In order to study the nature of the wave motion of the different parts (fields) of the sound-board of the pianoforte, when the same key on the key-board is pressed, the method adopted here is the same as the one already described in my previous paper. The following improvements are effected in the apparatus described therein. It was found that some friction acts between the surface of the fine cylindrical needle and the metallic support S as it was made of brass.[7] This friction, sometimes did not allow the needle to move freely and uniformly on the support. Therefore in order to avoid this friction, a glass slab is now attached to the upper surface of the support.

The electromagnetic arrangement formerly used for releasing the photographic plate when required, and for moving it at a uniform speed behind the slit S was somewhat complex, but now the arrangement is much simplified and is shown in Fig. 1 below.

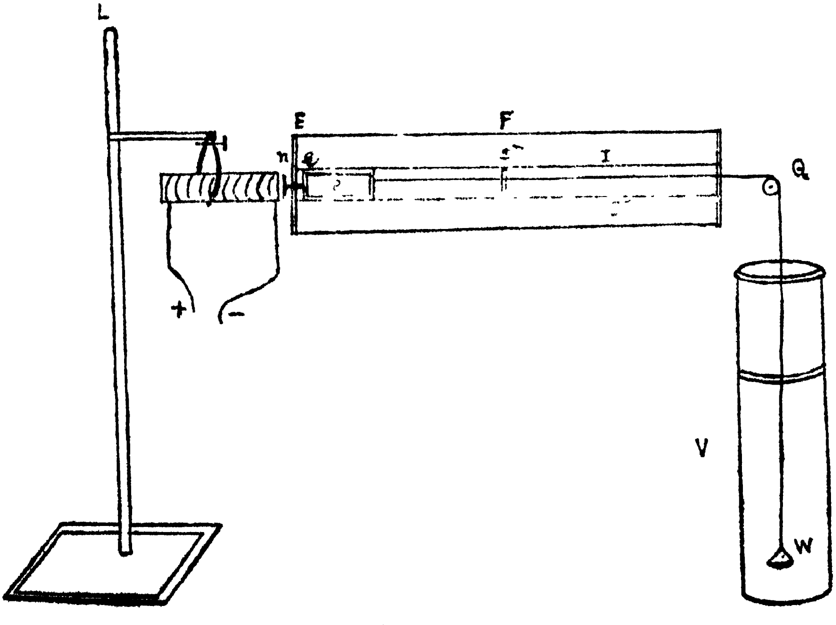

FIG. 1

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[7] See Fig. 1 on page 517, Ind. Jour. Phys., 4, (1930).

The plate P is held at the end E of the wooden frame F, and is released when desired, by the electromagnetic device, the construction of which is quite evident from the figure. Instead of using two electro-magnets, and a complex arrangement for letting loose the photographic plate, a simple cylindrical electromagnet is held by means of a wooden clamp and an iron stand. A soft iron nail (*n*) of wide flattened head is fixed into the nearer end (*c*) of the plate holder. The other end of the plate is tied to a string which is made to pass over a pulley Q and supported the weight W. When the electromagnet is excited, the iron nail head is attracted by it and the plate holder is thus held in position. When the current is stopped, the plate holder is let loose, and is moved towards the pulley Q, due to the weight W, attached to the other end of the string. The two rods I and I′ guide the motion of the plate holder. The weight W is made to move down in a cylindrical vessel V filled with oil in order to decrease the rate of motion of the plate on the frame F. The speed of this plate could thus be regulated and varied by varying the density of the liquid used in the vessel V.

The rest of the arrangement for the above and the electromagnetic arrangement for pressing any key of the keyboard are the same as those described in the previous paper.

3. *Construction of the Sound-Board used for the Experiment.*

The arrangement of the ribs on the sound board is different in different cases. The construction and the arrangement of the ribs on the sound board of the pianoforte which is used for the experiment is shown in Fig. 2. The arrangement illustrated in this figure is mostly prevalent at present for the position of the sounding board and ribs. The ribs are arranged in an inclined direction making an angle of about 60° with the horizontal plane of the pianoforte. These ribs divide the board into different fields. Thus all these ribs set

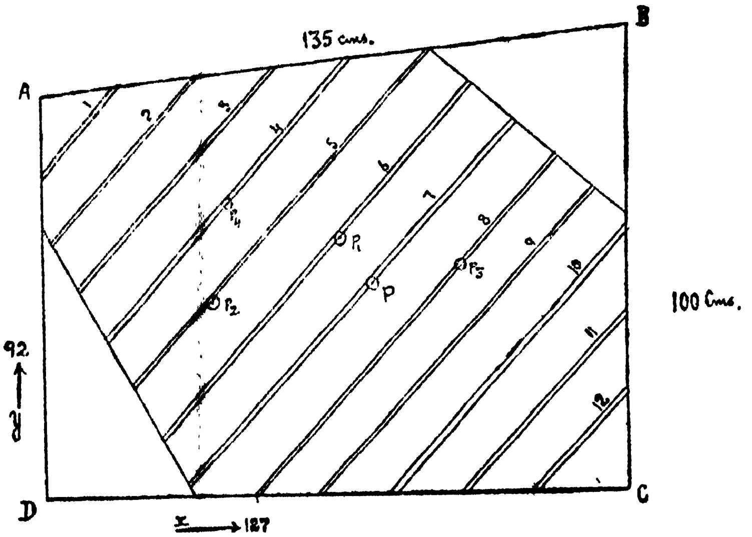

FIG. 2

the whole board into vibrations, almost diagonally, round the central rib. The following are the actual lengths in cms. of the ribs (the numbers are marked on the ribs in Fig. 2).

No. of the rib.	1	2	3	4	5	6	7	8	9	10	11	12
Length in cms.	25	48	68	80	96	109	110	90	84	71	60	54

The breadth and the thickness of almost all the ribs are about 2·5 cm. and the thickness of the longest rib is about 3·0 cm. The positions on the ribs where the clamp of the apparatus is attached have been fixed by the measurements of the cartesian co-ordinates with origin D in Fig. 2, and are tabulated below in Table I.

TABLE I.

Position	Cartesian Co-ordinates	Rib No. on which the point lies.
P	x = 55 cms. ; y = 35 cms.	7
P_1	= 47 ,, ; = 49 ,,	6
P_2	= 30 ,, ; = 33 ,,	5
P_3	= 77 ,, ; = 38 ,,	8
P_4	= 28 ,, ; = 51 ,,	4

4. *Results.*

Several curves showing the vibrations of the different parts of sound-board when the same key of the key-board is pressed have been photographed in this way keeping the magnification same (about 500 times approximately) in all the cases. The negatives of some of these curves have been enlarged on to the graph papers by the help of a projecting lantern, keeping the magnification same (5 times) in all the cases. They were then analysed by the mechanical process of Hawley O. Taylor.[8] A complete schedule for the analysis of the waves containing even as well as odd harmonics up to the 12th higher partial was utilised in calculating the overtones and their amplitudes present. The frequency of the key was found with a tuning fork by the beat method. The results obtained for some of the curves are tabulated in Table II.

TABLE II.

Frequency = 128	P	P_1	P_2	P_3	P_4
c_1	6·451	4·733	4·044	3·753	1·539
c_2	3·222	3·471	1·035	2·133	0·631
c_3	1·732	1·285	0·133	0·982	0·065
c_4	1·113	0·155	0·175	0·303	0·022
c_5	1·254	1·132	0·195	0·373	0·046
c_6	0·812	0·728	0·076	0·209	0·026
c_7	1·908	1·451	0·142	0·269	0·015
c_8	0·703	0·258	0·092	0·028	0·030
c_9	0·983	1·431	0·161	0·416	0·072
c_{10}	0·609	0·183	0·080	0·092	0·022
c_{11}	0·668	0·304	0·089	0·022	0·096
c_{12}	0·554	0·069	00·68	0·017	0·008

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[8] Phys. Rev., 6, 303 (1915).

In the above Table, c_1 is the fundamental and c_2, c_3, c_4, etc., are the overtones of the same, in each case. The amplitudes of the overtones are represented in centimeters. They are highly magnified but the magnification is the same in all cases. Hence the ratio of the amplitudes of all the harmonics in the curves remain the same. It does not interfere in the least with our results. From the results obtained by the mechanical analysis given in Table II, five curves are drawn showing the relation of the amplitude of the harmonics with their frequencies, and are shown in Fig. 3. The abscissa represents the frequencies of the harmonics and the ordinate their amplitudes in centimeters. To minimise the space and to understand better the internal of the keys, the frequencies are plotted on the octave scale. The confusion in the curves is avoided by plotting only a few curves for a certain key on the pianoscale. Thus curves 1, 2, 3, 4 and 5 respectively re-

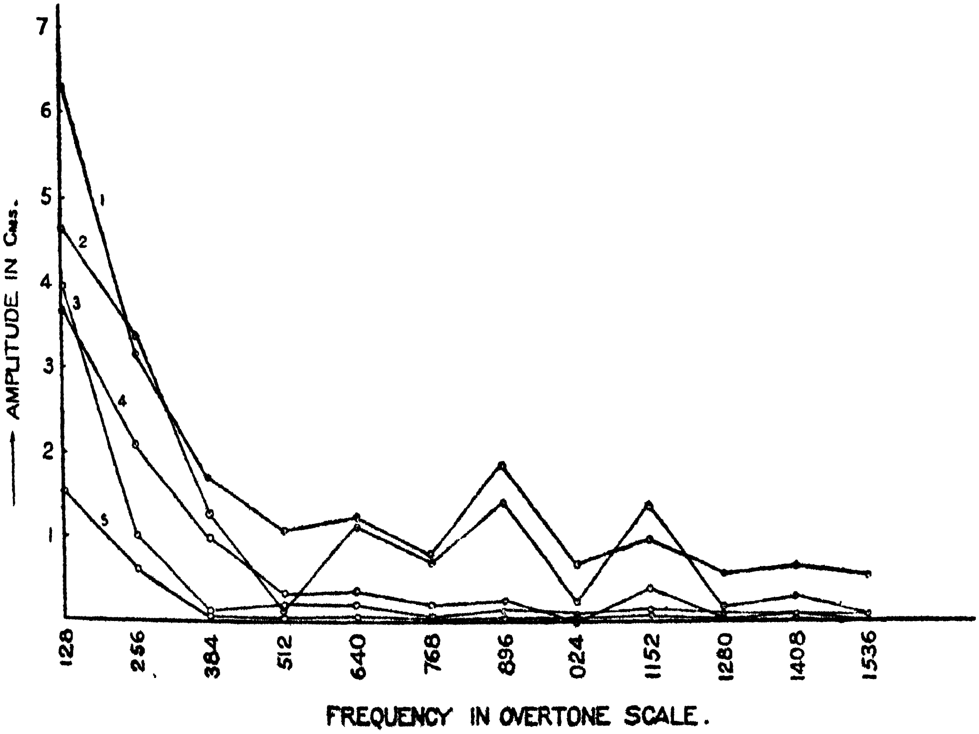

FIG. 3

present the amplitudes of the various harmonics present in the vibration curves of points p, p_1, p_2, p_3 and p_4 when the key of the frequency 128 per sec. is pressed on the pianoscale. In all the first three curves, there are five maxima present (1st, 5th, 7th, 9th and 11th). In curve No. 1 all the five are prominent whereas in 2 and 3 the first four are prominent. The amplitude of the 1st harmonic is very high in all the three cases. In curves 4 and 5 there are only four maxima instead of five as in the previous cases. In the case of curve 4 all the four maxima present (1st, 5th, 7th and 9th) are prominent whereas in the curve 5, out of the four maxima present (1st, 5th, 9th and 11th) only the fundamental is very prominent and all the rest die away very rapidly.

5. *Discussion of Results.*

The general appearance of the photographs obtained is the same for a given frequency except for a little variation in the amplitudes of different vibrations. Hence we can conclude that the nature of the vibration of all the points on the same sound-board, when any key of any frequency on the pianoscale is pressed, is the same except for slight variations in their amplitudes. Hence all points on the sound board have got the same kind of vibrations. The difference of amplitudes of vibrations is due to some other factor which is explained below.

Table II shows that the amplitude (A_p) of the fundamental harmonic of the vibration curve of point p is the maximum of all the fundamentals of the vibration curves of the other points. The amplitudes of the fundamentals of the vibration curves of other points are in the order $A_p > A_{p_1} > A_{p_2} > A_{p_3} > A_{p_4}$. Table III shows the corresponding lengths of the ribs, on which the points p, p_1, p_2, p_3 and p_4 lie.

TABLE III.

No. of the curve	1	2	3	4	5
No. of the point	p	p_1	p_2	p_3	p_4
Length of the rib in cms.	110	109	96	90	80
Amplitude of the fundamental in cms. (magnified)	6·451	4·733	4·044	3·753	1·539

It is clear from the above figures that the greater the length of the rib, the greater is the amplitude of the fundamental of the vibration of the rib. The exact relation of the amplitude of the fundamental of the vibration curve of any point on the sound-board, with the length of the rib on which the point lies, is shown below by a curve in Fig. 4. From

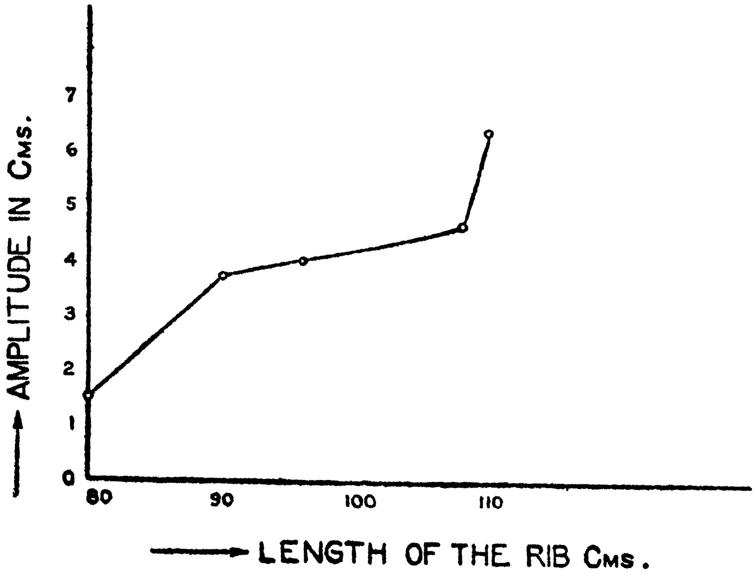

FIG. 4

what has been said above it may be concluded that the harmonics and maxima which are prominent in one curve, are also prominent in the other curves; or the vibrations of all the points on the various ribs are exactly similar in nature.

Hence vibrations of all ribs are exactly similar in nature. In general we may conclude that the whole sound-board vibrates as a whole in one piece round the ribs, though it consists of good many pieces of seasoned wood attached together and though the ribs divide the sound board into different fields. The ribbing divides the sound-board into fields, and through a correct relation of these field to one another, the degree of perfection of the resonance is partially determined. The sound-board is not alone given a certain stiffness by the ribbing, but its elasticity also stands in close connection with the same.

It may however be noted that in the curves corresponding to p_3 and p_4, the higher harmonics have disappeared. This shows that when the ribs of smaller length vibrate they do not produce higher harmonics of prominent amplitude. Thus in order to produce higher harmonics of prominent amplitude, the ribs of larger length are to be used. In order to increase the length of the ribs for a certain sound-board, the ribs are attached to the board diagonally, and not vertical or parallel to the foot of the pianoforte.

In conclusion the author desires to express his best and heartfelt thanks to Sir C. V. Raman, D.Sc., F.R.S., N.L., who provided facilities in his laboratory for photographing the vibration curves of the pianoforte sound-board.

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Intensity Relations in the Raman Spectrum of Hydrogen. II.

BY

S. BHAGAVANTAM.

(Plate XXXII.)

(*Received for publication, 21st December, 1932.*)

ABSTRACT.

An accurate determination is made of the intensity and polarisation characters of the various lines in the Raman spectrum of hydrogen gas. All the rotation lines are depolarised to the same extent, the value of ρ in each case being $0{\cdot}85 \pm 0{\cdot}05$. Their relative intensities are in good agreement with the conclusions of the quantum theory of the Raman effect developed by Manneback. The depolarisation of the vibration line $n: 0 \rightarrow 1$; $K: 1 \rightarrow 1$ is 0·13 and its intensity, expressed as a fraction of that of the corresponding Rayleigh line, is $2{\cdot}7 \times 10^{-3}$. The discrepancy, already reported in an earlier paper, between the experimental results and the conclusions of the theory in respect of the relative intensities of the Q and R branches of the vibration scattering has been confirmed. A preliminary investigation of the state of polarisation of the individual components of the Q branch shows that the line arising from molecules in the zero rotation state is depolarised to a certain extent. This result is not in agreement with the theory and has to be regarded as a further discrepancy.

1. *Introduction.*

In an earlier paper,[1] which will be referred to in the following pages as Part I, the author has described in detail the technique employed and the experimental results obtained in studying the intensity and polarisation characters exhibited by the Raman lines in the scattered spectrum of hydrogen gas. At that time, certain aspects of the problem such as the states of polarisation of the various lines had not however been investigated by the generally accepted methods in which use is made of the blackening-intensity curves for the photographic plate, and further, the results concerning the vibration line—its fine structure and intensity—were left incomplete. The importance of such investigations, particularly in a simple case like that of hydrogen, has led the author to repeat the entire work by the method of blackening-intensity curves and to extend the investigations so as to include the study of the fine structure and intensity of the vibration line as well. The new results are described in this part which may be regarded as a sequence to Part I and supplementing it in many respects.

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[1] Ind. Jour. Phys., 7, 107 (1932).

2. *Experimental Technique.*

The details of the construction of the gas container have already been described in Part I. The main improvements effected in the technique will be noted here. In Part I the horizontal and vertical components of the scattered light were photographed separately by inserting each time a suitably oriented nicol in front of the slit of the spectrograph. It is obvious, that under these conditions any fluctuations in the intensity of the lamp or a slight disturbance of the illuminating arrangements will interfere with the results. In order to overcome this difficulty in the present work, a double image prism is used to separate the two components which are then focussed on to the slit one above the other and the two spectra are thus simultaneously photographed. The ratio of intensities of the horizontal and vertical components of each one of the lines and of the various lines amongst themselves is in every case determined with the help of the blackening-intensity curves. The curves for any desired wave-length are obtained in the manner already described in Part I. It may be noted here that since in this case, the horizontal and the vertical components are both simultaneously exposed for identical periods, a correction due to the polarisation induced by oblique refraction at the prism surfaces has to be introduced in the final values. This correction factor is determined by a separate experiment. In Part I, it has been taken account of in the unequal times of exposure given for the two components. Another important source of error which needs to be carefully considered in a study of the state of polarisation of the well polarised Raman lines is a certain lack of transversality in the incident beam. This source of error has been dealt with in great detail in Part I, and it was shown that the use of a large condenser and a 6 inch long mercury arc introduces only an error of about +0·03 in the depolarisation values. The estimate was partly based on numerical calculations and partly on certain crucial experiments conducted regarding the depolarisation of the Rayleigh scattering by liquid CCl_4. It is however felt that the tests should be carried out afresh under conditions as nearly identical as possible with those prevailing in the actual experiments on gases. The experimental tube is therefore filled with methane gas at 40 atmospheres pressure and is illuminated by the light condensed from a 6 inch mercury arc by means of a condenser used in the experiments on hydrogen gas. The depolarisation of the scattered beam is determined under these conditions by the Cornu method, a large number of readings giving an average value of 0·065. Taking the standard value for methane as 0·015, it is seen that the error arising from oblique angles involved in the use of a long mercury arc, a large condenser, a thick walled quartz tube and possibly also from the presence of some parasitic light is only about +0·05 in the region of low depolarisation values. This result is very important in deciding upon the exact depolarisation of the vibration line, and will be used later in this connection. Unfortunately, it is not possible to obtain the vibration line with sufficient intensity in a reasonable time unless use is made of the above illuminating arrangements, and as such the correction involved becomes inevitable.

3. *Depolarisation of the Raman Lines.*

The figures contained in Table I give the depolarisation values for the rotation lines, and are obtained from two different plates. The average value of ρ comes out as 0·85.

Table I.—Depolarisation of the rotation lines.

Transition	K : 0 → 2	1 → 3	2 → 4	3 → 5
Depolarisation ρ Plate I	0·85	0·86	0·80	0·82
Depolarisation ρ Plate II	0·82	0·92	—	—

The depolarisation of the vibration line is determined on three different plates, and the values obtained range from 0·17 to 0·19. An upper limit of 0·05 is applied as a correction due to the lack of transversality in the incident beam as already explained, and the final value is given in column 4 of Table II.

TABLE II.—Depolarisation of the vibration line.

Transition.	Average observed ρ.	Correction due to angles, etc.	Corrected value of ρ.
K : 1 → 1 n : 0 → 1	0·18	0·05	0·13

4. *Relative Intensities of the Raman Lines.*

In Table III, the relative intensities of the various rotation lines are given. They represent the average of the figures obtained separately for the vertical and the horizontal components. As it has already been noted that the rotation lines are all depolarised to the same extent, it is clear that there should be no difference between the two cases. The figures are in good agreement with those contained in Part I.

TABLE III.—Relative intensities of rotation lines.

Transition.	K: 0→2.	1→3.	2→4.	3→5.
Intensity	0·73	2·0	0·31	0·24

A comparison is also made of the intensity of the vibration line with that of a vibration-rotation line in the horizontal component of the scattered beam. The following Table shows the results.

TABLE IV.—Relative intensities of vibration and vibration-rotation lines.

Transition. (Horizontal components.)	Relative intensities observed.	Relative intensities corrected.
K : 1→1 ; n : 0→1	1·6	1·2
K : 1→3 ; n : 0→1	0·8	0·8

In column 2 of the above Table, the observed intensities are given. It has already been pointed out that the apparent depolarisation of 0·18 exhibited by the vibration line has to be corrected to 0·13 in order to arrive at the true depolarisation and as such, the intensity of the horizontal component of the vibration line K: 1→1; n :0→1 as given in column 2 of Table IV has to be diminished in the ratio of 13/18 in order to eliminate the above source of error. The figures so corrected are contained in column 3 and are in good agreement with those already given in Part I. The important result to which attention may here be drawn is the larger intensity of the vibration line in comparison with that of the vibration-rotation line even after correcting for all the errors discussed above. This result has been clearly demonstrated in the reproduction of a microphotographic record already published in Part I, and is to be seen equally definitely on three other plates subsequently obtained by the author during the present investigation.

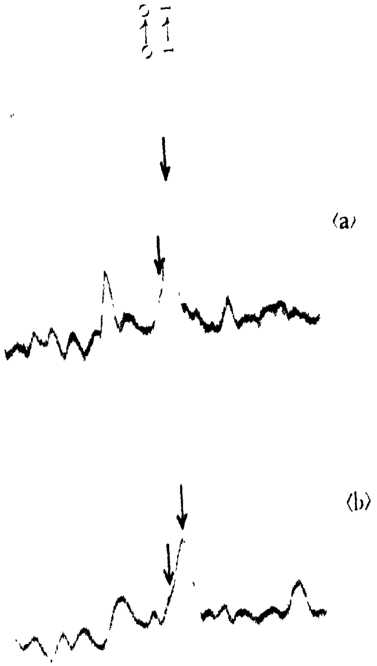
5. *Fine Structure of the Vibration Line.*

Vibration lines coming from molecules possessing different rotational energies do not coincide and as a result the Q branch consists of a number of closely spaced components, each one arising from a set of molecules in a particular rotational state. The distribution of intensity in the Q branch is thus largely dependent on the distribution of molecules over various rotational states and may easily be calculated on the basis of the Boltzmann law as has been done in Part I. In Table V, the observed intensities of the various lines in the vertical component of the scattered beam are given.

TABLE V.—Relative intensities of the fine structure components.

Transition n : 0→1.	K : 0→0.	1→1.	2→2.	3→3.
Intensity.	...	4·2	0·9	0·7

The figures are however not very accurate as the background for the two lines K : 2→2 and 3→3 becomes



(a) Vertical Component, (b) Horizontal Component

Fine structure of the vibration Raman line in hydrogen gas.

somewhat uncertain owing to the presence of the very intense line K : 1⟶1 in their close proximity. Nevertheless, they compare well with those given in Part I, and are in agreement with the theory. Although the line corresponding to K : 0⟶0 could be seen as a distinct peak in the microphotometric records, its intensity could not be estimated with any certainty. It has already been pointed out in Part I that the agreement with the Boltzmann distribution law need be expected in a general way to be fulfilled for the vertical components alone, and not for the horizontal components. The quantum theory developed by Manneback indicates that the first component, n : 0⟶1 ; K : 0⟶0, should be perfectly polarised while the higher ones corresponding to K : 1⟶1, 2⟶2 and 3⟶3 exhibit gradually increasing depolarisation values. This means that the line corresponding to n : 0⟶1 K : 0⟶0 should be altogether absent in the horizontal component of the scattered beam. In order to test the above results, photographs of the horizontal and vertical components of the Q branch have been separately obtained. Although the dispersion used is not sufficient to separate the various lines so well as to permit of an accurate determination of their relative intensities in each case, their presence is clearly seen in the microphotometric records obtained under favourable conditions. Figs. (*a*) and (*b*) of Plate XXXII represent respectively the structure of the vertical and horizontal components of the Q branch excited by λ3650. The exposure times are kept different in the two cases so as to make their intensities comparable. Contrary to the theoretical indications cited above, the peak corresponding to *n* : 0⟶1 ; K : 0⟶0 is noticeable equally well in both vertical and horizontal components as also the other peaks corresponding to K : 1⟶1, 2⟶2 and 3⟶3. The significance of this result will be discussed in a following section. It may however be noted here that an exact determination of the state of polarisation of each of the fine structure lines separately has not been possible, and the use of higher dispersion towards the solution of this problem is desirable.

6. *Intensity of the Vibration Line.*

In an earlier paper by the author,[2] an approximate estimate of the intensity of the vibration line in hydrogen in relation to the Rayleigh scattering was obtained by a direct comparison of the two. The procedure involved several corrections such as those due to the presence of parasitic light, widely different times of exposure, etc. It is proposed in this paper to make an accurate comparison of the intensity of the vibration line excited by λ 4046 with the rotation line $K:1 \longrightarrow 3$ excited by the same radiation. As in the foregoing cases, the relative intensities are obtained with the help of two different blackening-intensity curves drawn for the wavelengths λ 4145 (rotation line $K:1 \longrightarrow 3$ excited by λ 4046) and λ 4865 (vibration line $n:0 \longrightarrow 1$ excited by λ 4046). The ratio of the intensity of the vibration line to that of the Rayleigh line may be deduced from this result if the intensity of the rotation line in relation to that of the Rayleigh line is known. The results are given in Table VI.

TABLE VI.—Intensity of the Vibration Line.

Comparison.	$\dfrac{\text{Vibration line } (n:0 \longrightarrow 1)}{\text{Rotation line } (k:1 \longrightarrow 3)}$	$\dfrac{\text{Vibration line } (n:0 \longrightarrow 1)}{\text{Rayleigh line}}$	$\dfrac{\text{Vibration line} \left\lvert \begin{matrix} n:0 \longrightarrow 1 \\ k:1 \longrightarrow 1 \end{matrix} \right\rvert}{\text{Rayleigh line}}$
Relative Intensity.	0·26	$4{\cdot}2 \times 10^{-8}$	$2{\cdot}7 \times 10^{-3}$

The observed ratio of the intensities of the vibration line and the rotation line is given in column 2. The figure in column 3 is obtained by multiplying this by the ratio of the intensities of the rotation line and the corresponding Rayleigh line as determined in Part I. This however represents the total intensity of the Q branch and only a certain fraction of it will be attributable to the strongest component $n:0\longrightarrow 1$; $K:1\longrightarrow 1$. This figure is given in the last column and is in good agreement with the figure already reported (*loc. cit.* Ref. 2).

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[2] Ind. Jour. Phys., 6, 557 (1932).

7. *Discussion of the Results and Comparison with Theory.*

So far as the depolarisation values and the relative intensities of the various rotation lines are concerned, the results of this paper are in very good agreement with those already given in Part I and are to be expected on the basis of the quantum theory. For a detailed comparison of the experimental results with the theoretical conclusions in this respect reference may be made to Part I. The depolarisation of the vibration line is given in this paper as 0·13 and has been obtained after deducting 0·05 from the actually observed value 0·18 on account of a probable obliquity in the incident beam. The important result that the intensity of the horizontal component of the vibration line is nearly one and a half times as strong as the horizontal component of the vibration-rotation line even after correcting for the above error is practically a quantitative verification of the anomaly reported earlier in Part I. This experimental fact, which appears to be quite definite, is at variance with the theory and a tentative explanation based on the idea of a spinning photon has already been offered. Such a discrepancy is probably intimately connected with a further result obtained in the present work (see Sec. 5) regarding the fine structure components of the Q branch. The results of the quantum theory which are relevant in this connection will be briefly noted here. Molecules which are characterised by a rotational quantum number zero should give rise to a perfectly polarised Q branch. The observed depolarisation of the Q branch, if any, either in the Rayleigh scattering or in the vibration scattering, is to be attributed wholly to the radiation coming from molecules in higher rotational states. These statements may easily be verified from the detailed expressions given by Manneback for the intensity and polarisation of various lines. Contrary to the above conclusions, a separation of the Q branch in the vibration scattering into its various constituents, as explained in section 5, actually shows that part of its depolarisation has to be attributed to the radiation coming from molecules in the zero rotational state. In other words, the line $n: 0 \rightarrow 1$; $K: 0 \rightarrow 0$ exhibits a certain depolarisation although the molecules that scatter the light are both initially and finally in the zero rotational state. This result as also the previous one in which the depolarised part of the line $n: 0 \rightarrow 1$; $K: 1 \rightarrow 1$ was found to be stronger than the corresponding rotation line $n: 0 \rightarrow 1$; $K: 1 \rightarrow 3$ cannot be explained on the basis of the existing theory. It is necessary that some new mechanism has to be postulated which would give rise to an excess of the depolarised or the incoherent part of the Q branch in comparison with the P and R branches. The explanation offered in Part I is based on the idea that the light quantum has a certain spin whose sense at the time of the encounter in relation to that of the rotating molecule plays an important part if the result of such an encounter is to be treated as obeying the law of conservation of angular momentum. Such restrictions imposed on the encounter automatically result in the appearance of half or more than half of the unpolarised part of the scattered light in the form of a Q branch irrespective of what the quantum state of the scattering molecule is, and in this way both the above results may be accounted for.

It may however be noted here that some authors are of opinion that an experimental realisation of the angular momentum of a light quantum in any individual encounter is not possible on account of the principle of uncertainty coming into operation and as such, arguments of the preceding kind based on a detailed conservation of this quantity are defective. On the contrary, the fact that precisely such arguments lead to a simple and very straight-forward explanation of the selection rules and certain polarisation characters observed in the Raman effect appears to lend a strong support in their favour.

In conclusion, attention may be drawn to the extraordinarily large intensity of the vibration Raman line in hydrogen which is only about 1/300 of that of the corresponding Rayleigh line (See Table VI). Such intense lines are only apparently encountered in liquids where the coherent part of the Rayleigh scattering is considerably diminished by interference. Amongst gases however, hydrogen stands as an exception, as in all other cases investigated by the author, the Rayleigh line was found to be at least a few thousand times as strong as the vibration line. Such an exception is connected with the low moment of inertia of the hydrogen molecule and its consequently high rotation frequency. As a result of this, the parameter $x^2 = \nu_{rot} / \nu_{osc}$ entering into the expression for the intensity of the vibration line assumes a comparatively large value, and the line becomes very intense.[3] The other factor controlling the intensity of the vibration line, *viz.*, the variation of the optical polarisability with varying nuclear distance, is however of the same order of magnitude as in other diatomic gases such as O_2, N_2, etc.

The author desires to express his grateful thanks to Prof. Sir C. V. Raman for his kind interest in the work.

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[3] C. Manneback, Z. f. Phys., 62, 224 (1930).

41

"Further Investigation of the First Spark Spectrum of Arsenic"

By

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Plates XXXIII, XXXIV, and XXXV.

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Abstract.

By photographing the spectrum of arsenic under varying excitations in the region λ8400 to λ4000, the analysis of the lines of As II previously published by the writer, has been considerably extended. Higher members of the mp ^3P terms have been identified Combinations involving the transition of one of the inner group of s^2p^2 electron configuration have also been detected. Interesting cases of interpenetration of the different sub-levels, indicating a strong tendency towards the 'JJ' coupling is observed.

1. *Introduction.*

In continuation of the previous work by the writer on the First Spark Spectrum of Arsenic[1] the following paper gives an account of the extension of the regularities that have been discovered in the spectrum of As II. In addition to the deep 4p, 5s and 4d terms that were reported previously, all the terms of the 5p state, the $sp^3\ ^3P$, $sp^3\ ^3D$ and some of the 4f terms have been established in the present work.

2. *Experimental.*

The spark spectrum of arsenic has been photographed using varying degrees of excitation, in the region λ8400 to λ4000, by a glass Littrow spectrograph giving a dispersion of about 36A per mm. at λ6500 and 5·8A per mm. at λ4000. For the extreme red Kryptocynine plates were used and exposures of 6 to 8 hours were found necessary. Only two lines at about λ 7000, belonging to As III were recorded on these plates. The sources used in these experiments are the vacuum tube containing pure metallic arsenic and spark between electrodes of pure arsenic, in an atmosphere of hydrogen. The lines emitted by the latter source are generally very diffuse.

These experiments together with the work described in the previous paper[2] have led to the identification of the combinations of the 5p terms with those of the 4p and the sp^3 configurations.

3. *Structure of the Spectrum.*

The terms which are to be expected in the spectrum of As II, according to Hund's theory are shown in Table I.

Table I.—*Predicted Terms of As II.*

3_1	3_2	3_3	4_1	4_2	4_3	4_4	5_1	5_2	5_3	Term Prefix	Terms
2	6	10	2	2	..	·	--	---	--	4p	^3P ^1D ^1S
2	6	10	2	1	..	-	1	--	--	5s	^3P ^1P
2	6	10	2	1	1	—	-	—	..	4d	^3F ^3D ^3P ^1F ^1D ^1P
2	6	10	2	1	..		—	1	--	5p	^3D ^3P ^3S ^1D ^1P ^1S
2	6	10	2	1	...	1		-	-	4f	^3G ^3F ^3D ^1G ^1F ^1D
2	6	10	1	3	...	---	—	—	-	sp^3	^5S ^3D ^3P ^3S ^1D ^1P

All combinations identified in the spectrum of As II are given in Table II.

TABLE II.—*Combinations in As II.*

Terms			4p $^3P_0$	$^3P_1$	$^3P_2$	4p $^1D_2$	4p $^1S_0$
			162788	161725	160248	152693	140189
			1063	1477			
5s	$^3P_0$	84060·0		77665 (9)			
		397·4					
	$^3P_1$	83662·6	79128 (10)	78063 (8)	76586 (10)	69030 (3)	56527 (2)
		2380·3					
	$^3P_2$	81282·3		80445 (8)	78967 (10)	71112 (1)	
	$^1P_1$	79972·0	82816 (5)	81753 (2)	80278 (1)	72721 (10)	60219 (8)
4d	$^3F_2$	73960		87765 (2)	86285 (2)	—	
		720					
	$^3F_3$	73240			87007 (1)	79153 (2)	
	$^1F_3$	52916			107335 (1)	99771 (8)	
4d	$^3D_1$	63723	99065 (8)	98002 (6)	–	88961 (2)	76170 (4)
		483					
	$^3D_2$	63240		98485 (10)	97008 (3)	—	
		842					
	$^3D_3$	62398			97851 (10)	90291 (6)	
	$^1D_2$	60303		—	99941 (3)	92387 (10)	
4d	$^3P_0$	50547		111178 (1)			
		80					
	$^3P_1$	50467	112322 (0)	111258 (2)	109782 (1)	—	
		475					
	$^3P_2$	50942		110781 (2)	109309 (1)	101750 (0)	
	$^1P_1$	61302	101485 (1)	100423 (3)	98945 (2)	91391 (6)	78889 (10)
sp^3	$^3D_1$	89040·4	73745 (2)	—	—	63651 (1)	—
		112·5					
	$^3D_2$	88927·9		72799 (4)	—	63763 (2)	
		382·0					
	$^3D_3$	88545·9			71705 (3)	64148 (4)	

		4p $^3P_0$ *1063*	$^3P_1$ *1477*	$^3P_2$	4p $^1D_2$	4p $^1S_0$	5p $^3D_1$ *200·4*	$^3D_2$ *2083·5*	$^3D_3$	5p $^3P_0$ *942·5*	$^3P_1$ *1079·7*	$^3P_2$	5p $^3S_1$	5p $^1D_2$
		162788	161725	160248	152693	140189	65876·5	65676·1	63592·6	64552·9	63610·4	62530·7	61701·9	60399·4
P_0	78339		83386(2)											
	184													
$^1P_1$	78155	84634(3)	83570(1)	82092(1)	74537(1)	62030(1)								17755·8(3)
	470													
$^3P_2$	77685		84041(1)	82562(2)	...								15983·4(4)	17285·8(6)
$^1P_1$	79690	...	...	80561(3)	73004(8)	...						17159·2(3)	...	19291·0(7)
a	60193	...	101531(5)	100054(3)	92501(4)	79996(1)								
b	45047	117739(1)	116675(0)	...	107645(1)	95139(2)	20828·9(5)	20629·3(4)	...	19506·1(3)	18563·2(5)	...	...	15351·9(4)
c	43904	...	117822(1)	...	...	...	21972·5(4)	...	...	...	19707·2(2)	...	...	...
d	42019	121355(3)	120296(4)	...	...	98754(2)	23857·5(4)	23657·1(4)	...	...	21591·6(10)	...	19683·6(1)	18380·9(1)
e	41433	...	...	...	...	..	24443·8(2)	24243·2(3)	..	23119·7(8)	22177·0(7)	...	20269·1(3)	...
f	39004	...	...	...	121240(1)	113686(6)	26871·9(5)	...	...	...	24607·1(5)	23526·1(5)	22697·5(6)	21394·9(8)
g	38241	124549(2)	123486(5)	122011(7)	...	.	...	...	25351·2(2)	...	...	...	...	..
$^3P_2$	39565		122161(2)	120683(2)	113129(1)		26311·3(4)	26110·9(4)	24027·6(5)	...	24045·4(7)	22966·1(8)	22136·6(6)	...

TABLE II—*Continued.*

Multiplets due to the Transition 5p→5s.

Terms		5s $^3P_0$	*397·4*	$^3P_1$	*2380·3*	$^3P_2$	5s $^1P_1$
		84060·0		83662·6		81282·3	79972·0
5p $^3D_1$	65876·5	18183·5(10)		17786·1(4)		15405·6(2)	...
$^3D_2$	65676·1			17986·1(10)		15606·2(4)	...
$^3D_3$	63592·6					17689·4(10)	...
$^1D_2$	60399·4			23263·2(4)		20882·8(6)	19572·5(10)
5p $^3P_0$	64552·9			19109·7(8)			
$^3P_1$	63610·4	20449·5(8)		20052·8(8)		17671·7(8)	16361·3(10)
$^3P_2$	62530·7			21131·6(10)		18751·1(10)	17441·2(5)
$^1P_1$	67460·9	16599·0(10)		16201·8(10)		...	...
5p $^3S_1$	61701·9	22358·0(4)		21960·5(8)		19580·1(10)	18270·1(5)
$^1S_0$	57001·8			26660·8(9)			22970·2(10)

Multiplets due to Combinations between sp^3 ^{3}D and 5p Terms.

		sp^3 $^3D_1$	*112·6*	$^3D_2$	*382·0*	$^3D_3$
		89040·4		88927·9		88545·9
5p $^3D_1$	65876·5	23163·9 (8)		23051·7 (9)		
$^3D_2$	65676·1	23364·4 (4)		23251·9 (5)		22869·7 (8)
$^3D_3$	63592·6			25335·4 (3)		24953·4 (8)
$^1D_2$	60399·4			28528·2 (3)		23146·6 (4)
5p $^3P_0$	64552·9	24487·5 (6)				
$^3P_1$	68610·4	25429·8 (6)		25317·4 (8)		
$^3P_2$	62530·7	26510·0 (4)		26397·4 (6)		26015·2 (8)
5p $^3S_1$	61701·9	27388·7 (3)		27226·0 (5)		

Transition 4f→4d.

	$4f\ ^3F_2$	-55	$^3F_3$	1064	$^3F_4$	A	B
	41165		41220		40156	41269	41168
$4d\ ^3D_1$ 63723	22558·2 (10)					—	—
$^3D_2$ 63240	22075·7 (4)		22020·4 (10)			21972·5 (4)	—
$^3D_3$ 62398	—		21178·8 (2)		22242·7 (10)	—	21235·8 (10)
$^1D_2$ 60303	—		19083·5 (4)			19033·9 (3)	19139·8 (5)
$4d\ ^3F_2$ 73960	32795·0 (4)		32740·2 (4)			32690·8 (9)	—
$^3F_3$ 73240	—		32020·0 (4)		—	31970·6 (5)	32076·7 (10)

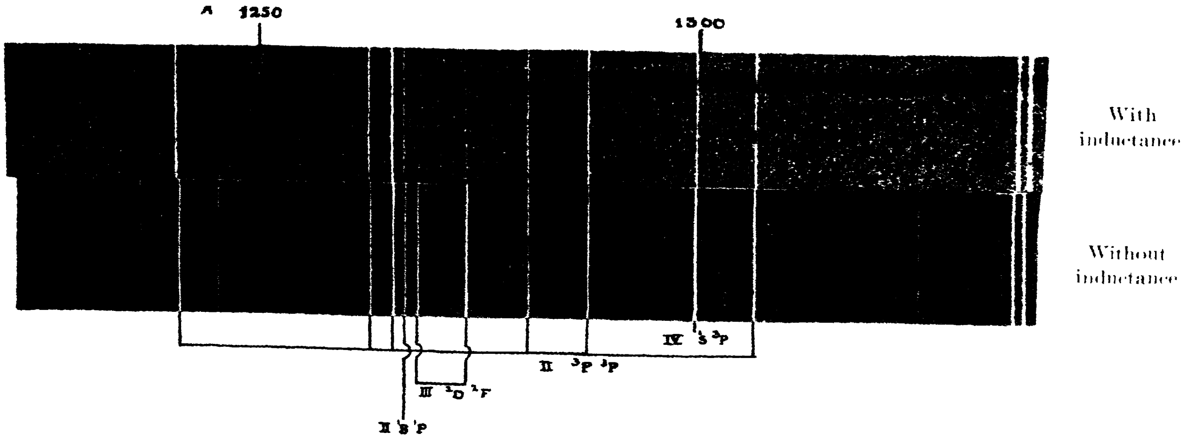
Other Regularities.

	C	D	E	F	G
	38723	38651	38582	37921	37545
$4d\ ^3D_2$ 63240	—	24590·1 (5)	—	—	25696·6 (3)
$^3D_3$ 62398	—	23747·9 (4)	23816·4 (7)	24478·1 (6)	24854·3 (8)
$^1D_2$ 60303	21579·8 (5)	21651·6 (5)	21720·2 (10)	22382·1 (9)	22756·4 (3)
$^1P_1$ 61302	22580·4 (10)	22650·7 (8)	—	—	23757·6 (7)
$4d\ ^3F_2$ 73960	—	35310·1 (8)	—	—	—
$^3F_3$ 73240	—	34589·4 (6)	34657·8 (8)	35319·7 (8)	—

The identification of the important triplet groups $4p\ ^3P - 5s\ ^3P$ and $4p\ ^3P - 4d\ ^3D$ is fully discussed in the former paper. These groups are shown in Plates XXXIII and XXXIV. The behaviour of the lines under different excitation unmistakably confirm the classifications of these lines.

Considering the new levels of the $4d$ state that have now been identified, the level $4d\ ^3F$ had to be located only by its combination with the deepest $4p$ terms. The intensities of such combination lines are usually faint. But the

PLATE XXXIII.



As. vac. spark.

identification of the *4d* ^{3}F term is based on the interval 720 Cm^{-1} (*4d* $^3F_2$—*4d* $^3F_3$) which is found to be a characteristic difference giving strong pairs in other regions of the spectrum.

The partial inversion of the *4d* ^{3}P term is in keeping with the corresponding term in Ge I and Se III[3]; but it is peculiar that the intensity of the line (*4p* $^3P_2$ – *4d* $^3P_2$) is abnormally low, while the inter-combination lines are much stronger.

All the terms of the *sp*^{3} configuration have not been detected. But the identification of *sp*^{3} ^{3}D is strongly supported by the existence of its combinations with the *4p* ^{3}P, *4p* ^{1}D and particularly with almost all the *5p* terms. The terms arising from this configuration, according to theory, are expected to show partial or complete inversion. If the identification suggested in the present work prove correct, both ^{3}P and ^{3}D are normal. The same feature is observed in the iso-electronic spectrum of Se III in the *sp*^{3} ^{3}D term. The *sp*^{3} ^{3}P, however is not definitely known in Ge I, while in Se III, it does show a partial inversion.

The spark spectrum of arsenic is exceedingly rich in lines in the visible and the quartz regions, which from experimental evidence, have to be assigned to the singly-ionised atom of the element. Our knowledge of the intervals of the 5s ^{3}P term affords a clue to the extension of the analysis of the spectrum into this region. A search for lines giving the difference 2380 and 397 cm^{-1} (equal to 5s $^3P_1$ – 5s $^3P_2$ and 5s $^3P_0$ – 5s $^3P_1$) has led to the identification of groups of terms due to the configuration *5p*. The location of the group 5s ^{3}P – *5p* ^{3}P at first presented considerable difficulties. In the former paper the level *ν*. 63610 was designated as *5p* $^1P_1$ as the intensity of the line λ 6110·30 was much larger than any of the other three lines λλ 5657·20, 4985·60, 4888·74. Adopting this designation the group 5s ^{3}P – 5p ^{3}P could not satisfactorily be located. A similar difficulty is met with in the spectrum of Se III (which was under investigation by Dr. J. S.

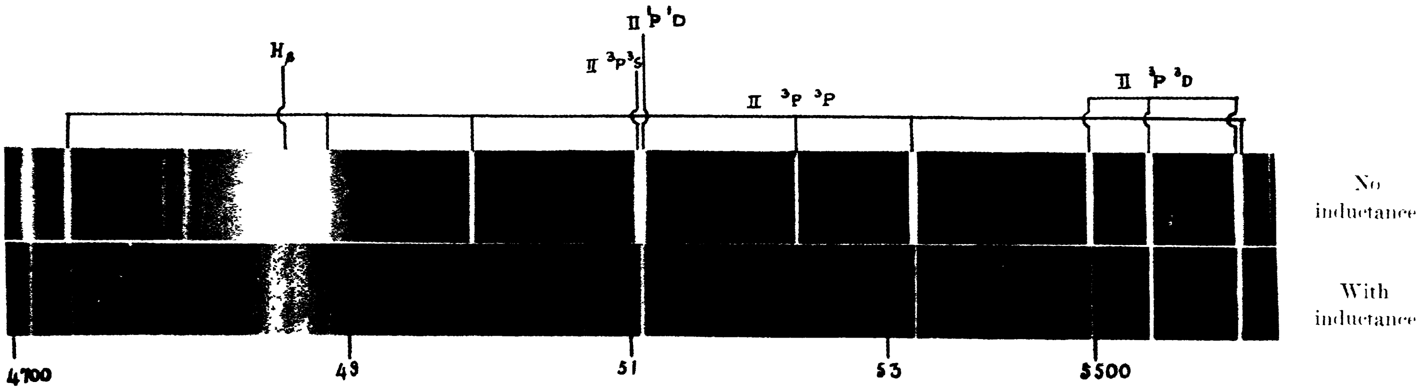
Badami and Dr. K. R. Rao and which has since been completed)[4] where the line ν. 24704·4 was found to be much stronger than any of the lines ν. 25969·3, 29578·9, 30083·0, of the $^3P\ ^3P$ combination. Therefore a change of 5p $^1P_1$ to 5p $^3P_1$ at once led to the identification of the group 5s $^3P - 5p\ ^3P$. This is further supported by the presence of the line λ6483·9 (5s $^1P_1 - 5p\ ^3P_0$), which appeared on two long exposure plates exactly at the predicted position. The magnitude and the ratio of the intervals of the component levels of the 5p ^3P term are perfectly regular and in complete agreement with the corresponding term in Se III. It is indeed very peculiar that the intercombination line 5s $^1P_1 - 5p\ ^3P_1$ is much stronger in the spectra of As II and Se III than the $^3P\ ^3P$ combinations.

TABLE III.

Spectrum	mp $\frac{^3P_1 - {^3P_2}}{^3P_0 - {^3P_1}}$	(m + 1)p $\frac{^3P_1 - {^3P_2}}{^3P_0 - {^3P_1}}$
C I	1·86	1·63
N II	1·68	1·66
O III	1·66	1·59
F IV	1·75	—
Si I	1·90	—
P II	1·84	8·17
S III	1·78	2·63
Cl IV	1·76	—
Ge I	1·53	—
As II	1·39	1·15
Se III	1·26	0·96
Br IV	0·92	0·95
Sn I	1·03	—
Sb II	0·85	—

RAO

PLATE XXXV.



As. spark in hydrogen.

Attention may here be drawn to the interesting variation of the interval ratio of the $mp\ ^3P$ terms in the spectra of the type under consideration. A progressive departure from the theoretical value of 2 :1 is observed with increase in the nuclear charge as is shown in Table III, indicating a gradual departure from the normal Russel-Saunders or (SL) type of coupling.

The ratio becomes less than unity in the $5p$ terms of Se III while in the case of Br IV this feature is noticed in the $4p$ terms themselves.

The terms $5p\ ^3D$, $5p\ ^3S$ and $5p\ ^1S$ were also located and a strong evidence in favour of the correctness of the identification of these levels is the detection of the complete multiplets arising from the combination of the $sp^3\ ^3D$ with terms of the $5p$ state. There is found to be good agreement in the position of these levels with the corresponding levels of Se III. The groups $5s\ ^3P-5p\ ^3D$ and $5s\ ^3P-5p\ ^3P$ are shown in Plate XXXV.

The identification of the $5p\ ^1So$ level is based on the separation 3690 cm^{-1} $(=5s\ ^3P_1-5s\ ^1P_1)$, as no other combinations with this level fall in the accessible regions. The level given in the previous paper by the writer had to be modified as the assignment of the line forming the combination $5s\ ^3P_1-5p\ ^1So$, to the first stage of ionisation of the atom was considered doubtful, on a further examination of the plates.

There is a strong pair in the red region λλ 6170 and 6022 belonging to As II with separation 397 cm^{-1} $(=5s\ ^3Po-5s\ ^3P_1)$, which has been chosen for the $5p\ ^1P_1$ level. This makes the value of this term $(=67461\ cm^{-1})$ higher than all the other $5p$ terms; but the identification is supported by the detection of a similar level in Se III, higher than the other $5p$ terms, for the $5p\ ^1P_1$. That the level should have an inner quantum number 1 receives support from the data on the hyperfine structure of these lines, studied independently by the writer[5] and by S. Tolansky.[6] Other combinations of this level with the 5s $^3P_2$ add 5s $^1P_1$, falling into the far red have not been detected.

There are still some strong lines of As II in the visible and the quartz regions which have not yet entered into the scheme developed above. These are believed to be due to the transition 4f ⟶ 4d of the series electron, which gives rise to multiplets of the type $^3D\ ^3F$, $^3D\ ^3D$, $^3P\ ^3D$, etc. The identification of these levels is found to be very difficult particularly in view of the fact that there is a good deal of uncertainty as regards the intervals which might be exhibited by the components of the 4f term. In no spectrum of the type of As II, hitherto investigated, have the 4f terms been identified. Attempts are therefore directed in the first instance towards detecting the regularities based on the equality of frequency differences. Such regularities are given in Table II, giving the chief multiplets of As II. Since the allocation of the various energy levels is found difficult, only arbitrary symbols have been used to designate them. But it is believed that these levels would prove to be those due to the 4 *f* configuration. The 4 *f* ^3F level has been tentatively suggested.

Attempts made to detect the higher members of the '*ms*' series of terms resulted in the identification of only the 6*s* $^3P_2$ level. No satisfactory level could be found for the 6*s* $^3P_1$ level.

4. *Term Values.*

An estimate of the term values of As II is made possible by the detection of two members of the *mp* ^3P, *mp* ^1D and also from the two members of the *ms* $^3P_2$ terms. By the application of the simple Rydberg formula the following limits are obtained.

$$5s\ ^1P_1 - 4p\ ^1D_2 = -\ 72724$$
$$5s\ ^1P_1 - 5p\ ^1D_2 = 19572.$$

The value of 5*s* $^1P_1$ derived from the above is 79975 cm^{-1}.

The triplet series $5s\ {}^3P_2 - 4p\ {}^3P_2 = -78967$; $5s\ {}^3P_2 - 5p\ {}^3P_2 = 18751$ gives the value of 80919 cm^{-1} for the $5s\ {}^3P_2$ level from which the $5s\ {}^1P_1 = 79609\ cm^{-1}$.

The values derived for the $5s\ {}^1P_1$ from the triplet and singlet systems are 79609 and 79975 cm^{-1} respectively. These are in close agreement with each other considering the probable error involved in the evaluation of these limits from a simple Rydberg formula. The latter value was adopted by the writer formerly before the triplet systems were identified. Since practically the same value is now obtained from the triplet system as well, no change has been made in the term values given in the former paper on As II. New levels identified since the completion of the above paper have also been evaluated. The deepest term is $4p\ {}^3P_0 = 162788\ cm^{-1}$ yielding a value of about 20·1 V for the ionisation potential of singly ionised As atom, which is in keeping with the following variation of the ionisation potential with atomic number.

7

TABLE IV.

C I	11·2	N II	29·5	O III	54·88
Si I	8·12	P II	19·81	S III	34·90
Ge I	8·09	As II	20·1	Se III	33·93

In Table V the term values in the iso-electronic spectra of Ge I, As II and Se III are given for purposes of comparison.

TABLE V.

Term Values in Se III, As II and Ge I.

Term	Se III		As II		Ge I	
	ν.	Δν.	ν.	Δν.	ν.	Δν.
4*p* $^3P_0$	274924	1741	162788	1063	65558·0	557·1
$^3P_1$	273183	2196	161725	1177	65000·9	852·8
$^3P_2$	270987		160248		64148·1	
$^1D_2$	261892		152693		58432·8	
$^1S_0$	...		140189		...	
sp^3 $^3D_1$	183833	1632	89040·4	112·5	5833·3	- 36·6
$^3D_2$	182201	3825	88927·9	382·0	5869·9	— 33·0
$^3D_3$	178376		88545·9		5902·9	
$^3P_0$	168442	109	78339	184	7882·9	—278·0
$^3P_1$	168333	—76	78155	470	8160·9	—742·2
$^3P_2$	168409		77685		8903·1	
$^1P_1$	...		79690		0084·4	
5*s* $^3P_0$	148647·1	504·5	84060·0	397·4	28106·43	250·59
$^3P_1$	148142·6	3609·6	83662·6	2380·3	27855·81	1115·51
$^3P_2$	144533·0		81282·3		26410·33	
$^1P_1$	143268·1		79972·0		25537·65	
4*d* $^3F_2$	135663·7	1257·9	73962	722	15489·3	254·1
$^3F_3$	134405·8		73240		15235·2	
$^1F_3$	126249		52916		12966·0	
$^3D_1$	134284·3	—1230	63723	483	16595·7	—80·4
$^3D_2$	135514·3	2604·9	63240	842	16676·1	262·2
$^3D_3$	132909·4		62398		16413·9	
$^1D_2$	135720·3		60303		17078·3	
$^3P_0$	132608·2	442·4	50547	80	13578·2	—275·2
$^3P_1$	132165·8	—52·1	50467	—475	13853·4	—267·2
$^3P_2$	132217·9		50942		14120·6	
$^1P_1$	137977·5		61302		12711·0	

Term.	Se III		As II		Ge. I	
	ν	$\Delta\nu$.	ν.	$\Delta\nu$	ν.	$\Delta\nu$.
$5p\ ^3D_1$	121712·6	309·5	65876·5	200·4	...	
$^3D_2$	121403·1	3172·0	65676·5	2083·5	...	
$^3D_3$	118231·1		63592·6		...	
$^1D_2$	113753·8		60399·4		.	
$^3P_0$	120141·0		64552·9			
$^3P_1$	118563·6	1577·4	63610·4	942·5		
$^3P_2$	117049·8	1513·8	62530·7	1079·7	...	
$^1P_1$	121162·9		67160·9		.	
$^3S_1$	115621·1		61701·9		..	
$^1S_0$	...		57001·8		...	
$6s\ ^3P_2$	...		39565		13387·7	

Other Energy Levels of As II.

Term	Term Value	Term	Term Value
a	60193	$4f\ ^3F_3$	40156
b	45047	f	39004
c	43904	C	38723
d	42019	D	38651
e	41483	E	38582
A	41269	g	38241
$4f\ ^3F_3$	41220	F	37921
$^3F_2$	41165	G	37545
B	41163	...	...

From the above comparison between the energy levels of Ge I, As II and Se III, it is seen that the relative positions of the terms due to the sp^3 configuration with respect to those of

the 4d or the 5s state gradually increase as we proceed from Ge I to Se III.

Another interesting feature to be noticed about the energy levels is that the intervals of certain terms of the 4d and the 5p states are large compared with the separations between the terms themselves so that the different terms interpenetrate into each other, as for example the 5p ^3P, 5p ^3D of As II, etc. In the case of Se III also this feature is markedly seen.

Finally in Table VI is given a catalogue of all lines that have been ascribed to the singly-ionised atom of arsenic together with the classification of the lines that have been analysed in the present investigation.

TABLE VI.

Catalogue of As II Lines.

λ	ν	Classification
6528·06 (3)	15314·3	...
6512·42 (4)	15351·0	$5p^1D_2-G$
6489·35 (2)	15405·6	$5s^3P_2-5p^3D_1$
6483·86 (2)	15418·7	$5s^1P_1-5p^3P_0$
6443·96 (2)	15514·1	...
6430·00 (0)	15547·8	...
6405·95 (4)	15606·2	$5s^3P_2-5p^3D_2$
6254·77 (4)	15983·4	$sp^{33}P_2-5p^3S_1$
6170·47 (10)	16201·8	$5s^3P_1-5p^1P_1$
6136·01 (5)	16292·7	...
6110·30 (10)	16361·3	$5s^1P_1-5p^3P_1$
6081·06 (2)	16440·0	...
6076·82 (5)	16451·4	...
6073·63 (1)	16460·1	...
6022·81 (10)	16599·0	$5s^3P_0-5p^1P_1$

λ	ν	Classification
5972·34 (3)	16739·2	...
5966·79 (2)	16754·8	...
5838·19 (9)	17123·9	...
5826·15 (3)	17159·2	$sp^3\ {}^1P_1 - 5p\ {}^3P_2$
5783·51 (6)	17285·8	$sp^3\ {}^3P_2 - 5p\ {}^1D_2$
5731·96 (5)	17441·2	$5s\ {}^1P_1 - 5p\ {}^3P_2$
5685·74 (8)	17583·0	...
5657·20 (8)	17671·7	$5s\ {}^3P_2 - 5p\ {}^3P_1$
5651·53 (10)	17689·4	$5s\ {}^3P_2 - 5p\ {}^3D_3$
5630·42 (3)	17755·8	$sp^3\ {}^3P_1 - 5p\ {}^1D_2$
5620·82 (4)	17786·1	$5s\ {}^3P_1 - 5p\ {}^3D_1$
5558·31 (10)	17986·1	$5s\ {}^3P_1 - 5p\ {}^3D_2$
5497·98 (10)	18183·5	$5s\ {}^3P_0 - 5p\ {}^3D_1$
5497·09 (4)	18186·4	—
5491·81 (4)	18203·9	—
5471·92 (5)	18270·1	$5s\ {}^1P_1 - 5p\ {}^3S_1$
5451·40 (2)	18338·8	—
5438·92 (1)	18380·9	$5p\ {}^1D_2 - d$
5385·52 (5)	18563·2	$5p\ {}^3P_1 - b$
5331·54 (10)	18751·1	$5s\ {}^3P_2 - 5p\ {}^3P_2$
5252·32 (3)	19033·9	$4d\ {}^1D_2 - A$
5238·69 (4)	19083·5	$4d\ {}^1D_2 - 4f\ {}^3F_3$
5231·50 (8)	19109·7	$5s\ {}^3P_1 - 5p\ {}^3P_0$
5223·27 (5)	19139·8	$4d\ {}^1D_2 - B$
5215·56 (3)	19168·1	—
5205·40 (4)	19205·5	—
5182·32 (7)	19291·0	$sp^3\ {}^1P_1 - 5p\ {}^1D_2$
5161·25 (7)	19369·8	—
5125·18 (3)	19506·1	$5p\ {}^3P_0 - b$
5107·80 (10)	19572·5	$5s\ {}^1P_1 - 5p\ {}^1D_2$

λ	ν	Classification
5105·80 (10)	19580·1	$5s\,^3P_2$—$5p\,^3S_1$
5072·07 (2)	19707·2	$5p\,^3P_1$—c
4985·60 (8)	20052·2	$5s\,^3P_1$—$5p\,^3P_1$
4932·24 (3)	20269·1	$5p\,^3S_1$—e
4888·74 (8)	20449·5	$5s\,^3P_0$—$5p\,^3P_1$
4846·13 (4)	20629·3	$5p\,^3D_2$—b
4812·01 (4)	20775·6	—
4802·25 (5)	20817·8	—
4799·68 (5)	20828·9	$5p\,^3D_1$—b
4787·29 (6)	20882·8	$5s\,^3P_2$—$5p\,^1D_2$
4730·92 (10)	21131·6	$5s\,^3P_1$—$5p\,^3P_2$
4720·38 (2)	21178·8	$4d\,^3D_3$—$4f\,^3F_3$
4707·82 (10)	21235·3	$4d\,^3D_3$—B
4672·70 (8)	21394·9	$5p\,^1D_2$—f
4648·82 (7)	21507·1	—
4632·67 (5)	21579·8	$4d\,^1D_2$—C
4630·14 (10)	21591·6	$5p\,^3P_1$—d
4627·80 (10)	21602·5	—
4619·63 (4)	21640·7	—
4617·30 (5)	21651·6	$4d\,^1D_2$—D
4607·46 (10)	21697·9	—
4602·73 (10)	21720·2	$4d\,^1D_2$—E
4591·02 (7)	21775·6	—
4582·50 (2)	21816·1	...
4580·92 (4)	21823·6	...
4574·80 (2)	21852·8	...
4574·18 (2)	21855·7	...
4567·95 (3)	21885·5	...
4560·27 (2)	21922·4	...
4552·37 (8)	21960·5	$5s\,^3P_1$—$5p\,^3S_1$

λ	ν	Classification
4549·87 (4)	21972·5	$4d\ ^3D_2-A$
4549·23 (10)	21975·6	...
4543·76 (10)	22002·1	...
4539·97 (10)	22020·4	$4d\ ^3D_2-4f\ ^3F_3$
4532·36 (4)	22057·4	...
4528·61 (4)	22075·7	$4d\ ^3D_2-4f\ ^3F_2$
4516·14 (6)	22136·6	$5p\ ^3S_1-6s\ ^3P_2$
4509·33 (5)	22170·1	...
4507·92 (7)	22177·0	$5p\ ^3P_1-e$
4494·59 (10)	22242·7	$4d\ ^3D_3-4f\ ^3F_4$
4475·69 (7)	22336·7	...
4474·60 (10)	22342·1	...
4471·43 (4)	22358·0	$5s\ ^3P_0-5p\ ^3S_1$
4469·02 (1)	22370·0	...
4466·60 (9)	22382·1	$4d\ ^1D_2-F$
4461·92 (4)	22405·6	...
4461·27 (7)	22408·9	...
4460·29 (5)	21413·8	...
4458·74 (7)	22421·6	...
4456·86 (6)	22431·0	...
4447·62 (2)	22477·6	...
4431·73 (10)	22558·2	$4d\ ^3D_1-4f\ ^3F_2$
4427·38 (10)	22580·4	$4d\ ^1P_1-C$
4421·06 (5)	22612·7	...
4413·64 (8)	22650·7	$4d\ ^1P_1-D$
4412·25 (5)	22657·8	...
4404·53 (6)	22697·5	$5p\ ^3S_1-f$
4392·76 (3)	22758·4	$4d\ ^1D_2-G$
4371·38 (8)	22869·7	$sp^3\ ^3D_3-5p\ ^3D_2$
4367·10 (3)	22892·1	...

λ	ν	Classification
4359·90 (4)	22929·9	...
4353·02 (8)	22966·1	$5p\ ^3P_2-6s\ ^3P_2$
4352·25 (10)	22970·2	$5s\ ^1P_1-5p\ ^1S_0$
4336·85 (9)	23051·7	$sp^3\ ^3D_2-5p\ ^3D_1$
4324·10 (8)	23119·7	$5p\ ^3P_0-e$
4315·86 (8)	23163·9	$sp^3\ ^3D_1-5p\ ^3D_1$
4302·26 (3)	23237·1	...
4299·51 (5)	23251·9	$sp^3\ ^3D_1-5p\ ^3D_2$
4297·43 (4)	23263·2	$5s\ ^3P_1-5p\ ^1D_2$
4278·82 (4)	23364·4	$sp^3\ ^3D_1-5p\ ^3D_2$
4267·24 (2)	23427·8	...
4265·13 (7)	23439·4	...
4249·40 (5)	23526·1	$5p\ ^3P_2-f$
4243·26 (9)	23560·2	...
4228·42 (5)	23642·9	...
4225·87 (4)	23657·1	$5p\ ^3D_2-d$
4221·23 (3)	23683·1	...
4209·71 (4)	23747·9	$4d\ ^3D_2-D$
4208·00 (7)	23757·6	$4d\ ^1P_1-G$
4197·61 (7)	23816·4	$4d\ ^3D_3-E$
4190·37 (4)	23857·5	$5p\ ^3D_1-d$
4160·72 (5)	24027·6	$5p\ ^3D_3-6s\ ^3P_2$
4157·64 (7)	24045·4	$5p\ ^3P_1-6s\ ^3P_2$
4123·71 (3)	24243·2	$5p\ ^3D_2-e$
4119·85 (8)	24265·9	...
4089·87 (2)	24443·8	$5p\ ^3D_1-e$
4084·13 (6)	24478·1	$4d\ ^3D_3-F$
4083·01 (1)	24484·8	...
4082·57 (6)	24487·5	$sp^3\ ^3D_1-5p\ ^3P_0$
4077·08 (4)	24520·5	...

λ	ν	Classification
4071·64 (4)	24553·2	...
4070·92 (4)	24557·6	...
4065·54 (5)	24590·1	$4d\ {}^3\mathrm{D}_2-\mathrm{D}$
4062·73 (5)	24607·1	$5p\ {}^3\mathrm{P}_1-f$
4022·32 (3)	24854·3	$4d\ {}^3\mathrm{D}_3-\mathrm{G}$
4006·34 (8)	24953·4	$sp^3\ {}^3\mathrm{D}_3-5p\ {}^3\mathrm{D}_3$
3982·45 (7)	25103·1	—
3948·74 (8)	25317·4	$sp^3\ {}^3\mathrm{D}_2-5p\ {}^3p_1$
3945·93 (4)	25335·4	$sp^3\ {}^3\mathrm{D}_2-5p\ {}^3\mathrm{D}_3$
3943·47 (2)	25351·2	$5p\ {}^3\mathrm{D}_3-g$
3931·28 (6)	25429·8	$sp^3\ {}^3\mathrm{D}_1-5p\ {}^3\mathrm{P}_1$
3927·96 (2)	25451·3	—
3896·21 (0)	25658·7	—
3890·46 (3)	25696·6	$4d\ {}^3\mathrm{D}_2-\mathrm{G}$
3842·82 (8)	26015·2	$sp^3\ {}^3\mathrm{D}_3-5p\ {}^3\mathrm{P}_2$
3841·03 (4)	26027·2	—
3828·74 (4)	26110·9	$0p\ {}^3\mathrm{D}_2-6s\ {}^3\mathrm{P}_2$
3804·16 (1)	26279·6	—
3799·58 (4)	26311·3	$5p\ {}^3\mathrm{D}_1-6s\ {}^3\mathrm{P}_2$
3787·18 (6)	26397·4	$sp^3\ {}^3\mathrm{D}_2-5p\ {}^3\mathrm{P}_2$
3771·10 (4)	26510·0	$sp^3\ {}^3\mathrm{D}_1-5p\ {}^3\mathrm{P}_2$
3749·77 (9)	26660·8	$5s\ {}^3p_1-5p\ {}^1\mathrm{So}$
3720·31 (5)	26871·9	$5p\ {}^3\mathrm{D}_1-f$
3683·58 (5)	27139·8	—
3671·92 (5)	27226·0	$sp^3\ {}^3\mathrm{D}_2-5p\ {}^3\mathrm{S}_1$
3656·78 (3)	27338·7	$sp^3\ {}^3\mathrm{D}_1-5p\ {}^3\mathrm{S}_1$
3551·82 (4)	28146·6	$sp^3\ {}^3\mathrm{D}_3-5p\ {}^1\mathrm{D}_2$
3549·02 (1)	28168·8	—
3545·77 (3)	28194·6	—
3513·18 (3)	28456·5	—

λ	ν	Classification
3504·30 (3)	28528·2	sp^3 $^3D_2$—$5p$ $^1D_2$
3126·97 (5)	31970·6	$4d$ $^3F_3$—A
3122·15 (4)	32020·0	$4d$ $^3F_3$—$4f$ $^3F_3$
3116·63 (10)	32076·7	$4d$ $^3F_3$—B
3058·08 (9)	32690·8	$4d$ $^3F_2$—A
3053·46 (9)	32740·2	$4d$ $^3F_2$—$4f$ $^3F_3$
3048·36 (4)	32795·0	$4d$ $^3F_2$—$4f$ $^3F_2$
3003·93 (8)	33280·1	—
2959·70 (10)	33777·4	—
2890·21 (6)	34589·4	$4d$ $^3F_3$—D
2884·51 (8)	34657·8	$4d$ $^3F_3$—E
2831·22 (1)	35310·1	$4d$ $^3F_2$—D
2830·45 (8)	35319·7	$4d$ $^3F_3$—F
2790·28 (3)	35828·1	—
2741·38 (2)	36467·2	—
2733·30 (2)	36575·0	—
2713·97 (1)	36835·5	—
2602·96 (7)	38406·3	—
2577·21 (3)	38790·0	—
2573·25 (4)	38849·7	—
2561·18 (4)	39032·8	—
2537·79 (4)	39392·5	—
2498·25 (4)	40015·9	—
2490·44 (2)	40141·4	—
2465·65 (3)	40545·0	—
2463·89 (3)	40573·9	—
2461·76 (3)	40609·1	—
2445·65 (3)	40876·5	—
2436·00 (4)	41038·5	—
2433·76 (5)	41076·2	—

λ	ν	Classification
2361·42 (2)	42334·4	—
1769·06 (2)	56527	$4p\ ^1S_0-5s\ ^3P_1$
1660·60 (8)	60219	$4p\ ^1S_0-5s\ ^3P_1$
1612·11 (1)	62030	$4p\ ^1S_0-sp^3\ ^3P_1$
1571·05 (2)	63651	$4p\ ^1D_2-sp^3\ ^3D_1$
1568·30 (2)	63763	$4p\ ^1D_2-sp^3\ ^3D_2$
1558·88 (4)	64148	$4p\ ^1D_2-sp^3\ ^3D_3$
1448·64 (1)	69030	$4p\ ^1D_2-5s\ ^3P_2$
1400·32 (4)	71412	$4p\ ^1D_2-5s\ ^3P_2$
1394·61 (4)	71705	$4p\ ^3P_2-sp^3\ ^3D_3$
1375·07 (10)	72724	$4p\ ^1D_2-5s\ ^1P_1$
1373·65 (4)	72799	$4p\ ^3P_1-sp^3\ ^3D_2$
1369·78 (5)	73004	$4p\ ^1D_2-sp^3\ ^1P_1$
1356·02 (3)	73745	$4p\ ^3P_0-sp^3\ ^3D_1$
1341·53 (1)	74537	$4p\ ^1D_2-sp^3\ ^3P_1$
1307·76 (8)	76470	$4p\ ^1S_0-4d\ ^3D_1$
1305·72 (10)	76586	$4p\ ^3P_2-5s\ ^3P_1$
1287·57 (9)	77666	$4p\ ^3P_1-5s\ ^3P_0$
1281·01 (8)	78063	$4p\ ^3P_1-5s\ ^3P_1$
1267·61 (10)	78889	$4p\ ^1S_0-4d\ ^1P_1$
1266·36 (10)	78967	$4p\ ^3P_2-5s\ ^3P_2$
1263·78 (10)	79128	$4p\ ^3P_0-5s\ ^3P_1$
1258·61 (2)	79453	$4p\ ^1D_2-4d\ ^3F_3$
1250·07 (1)	79996	$4p\ ^1S_0-a$
1245·67 (1)	80278	$4p\ ^3P_2-5s\ ^1P_1$
1243·09 (8)	80445	$4p\ ^3P_1-5s\ ^3P_2$
1241·29 (3)	80561	$4p\ ^3P_2-sp^3\ ^1P_1$
1223·19 (2)	81753	$4p\ ^3P_1-5s\ ^1P_1$
1218·14 (1)	82092	$4p\ ^3P_2-sp^3\ ^3P_1$
1211·21 (2)	82562	$4p\ ^3P_2-sp^3\ ^3P_2$

λ	ν	Classification
1207·50 (5)	82816	$4p\ ^3P_0 - 5s\ ^1P_1$
1199·24 (2)	83386	$4p\ ^3P_1 - sp^3\ ^3P_0$
1196·60 (1)	83570	$4p\ ^3P_1 - sp^3\ ^3P_1$
1189·90 (1)	84041	$4p\ ^3P_1 - sp^3\ ^3P_2$
1181·55 (3)	84634	$4p\ ^3P_0 - sp^3\ ^3P_1$
1158·95 (2)	86285	$4p\ ^3P_2 - 4d\ ^3F_2$
1149·33 (4)	87007	$4p\ ^3P_2 - 4d\ ^3F_3$
1139·40 (2)	87765	$4p\ ^3P_1 - 4d\ ^3F_2$
1124·05 (2)	88964	$4p\ ^1D_2 - 4d\ ^3D_1$
1107·49 (6)	90294	$4p\ ^1D_2 - 4d\ ^3D_3$
1094·20 (6)	91391	$4p\ ^1D_2 - 4d\ ^1P_1$
1082·40 (10)	92387	$4p\ ^1D_2 - 4d\ ^1D_2$
1081·07 (4)	92501	$4p\ ^1D_2 - a$
1051·09 (2)	95139	$4p\ ^1S_0 - b$
1030·84 (2)	97008	$4p\ ^3P_2 - 4d\ ^3D_2$
1021·96 (10)	97851	$4p\ ^3P_2 - 4d\ ^3D_3$
1020·39 (6)	98002	$4p\ ^3P_1 - 4d\ ^3D_1$
1015·38 (10)	98485	$4p\ ^3P_1 - 4d\ ^3D_2$
1012·62 (2)	98754	$4p\ ^1S_0 - d$
1010·66 (2)	98945	$4p\ ^3P_2 - 4d\ ^1P_1$
1009·44 (8)	99065	$4p\ ^3P_0 - 4d\ ^3D_1$
1002·27 (8)	99774	$4p\ ^1D_2 - 4d\ ^1F_3$
1000·56 (3)	99944	$4p\ ^3P_2 - 4d\ ^1D_2$
999·46 (3)	100054	$4p\ ^3P_2 - a$
995·79 (3)	100423	$4p\ ^3P_1 - 4d\ ^1P_1$
985·37 (4)	101487	$4p\ ^3P_0 - 4d\ ^1P_1$
984·92 (5)	101531	$4p\ ^3P_1 - a$
982·80 (0)	101750	$4p\ ^1D_2 - 4d\ ^3P_2$
931·66 (1)	107335	$4p\ ^3P_2 - 4d\ ^1F_3$
928·98 (1)	107645	$4p\ ^1D_2 - b$

λ	ν	Classification
914·84 (1)	109309	$4p\ {}^3P_2-4d\ {}^3P_2$
910·90 (4)	109782	$4p\ {}^3P_2-4d\ {}^3P_1$
902 68 (2)	110781	$4p\ {}^3P_1-4d\ {}^3P_2$
899·46 (1)	111178	$4p\ {}^3P_1-4d\ {}^3P_0$
898·81 (2)	111258	$4p\ {}^3P_1-4d\ {}^3P_1$
890·30 (1)	112322	$4p\ {}^3P_0-4d\ {}^3P_1$
883·95 (1)	113129	$4p\ {}^1D_2-6s\ {}^3P_2$
879·62 (6)	113686	$4P\ {}^1S_0-f$
857·07 (0)	116675	$4p\ {}^3P_1-b$
849·31 (1)	117739	$4p\ {}^3P_0-b$
848·74 (1)	117822	$4p\ {}^3P_1-c$
831·28 (1)	120296	$4p\ {}^3P_1-d$
828·62 (2)	12066	$4p\ {}^3P_2-6s\ {}^3P_2$
824·81 (1)	121240	$4p\ {}^1D_2-f$
824·03 (3)	121355	$4p\ {}^3P_0-d$
819·60 (7)	122011	$4p\ {}^3P_2-g$
818·59 (2)	122161	$4p\ {}^3P_1-6s\ {}^3P_2$
809·81 (5)	123486	$4p\ {}^3P_1-g$
802·90 (2)	124549	$4p\ {}^3P_0-g$

Summary and Conclusions.

The spectrum of arsenic has been studied under varying excitations and about 280 lines have been ascribed to the singly ionised atom of arsenic, a large number of these having been classified. Combinations between the deep terms of the singlets and triplet system of As II and higher members of the $mp\ {}^3P$ terms have been identified. Terms due to the 4*d* and 4f configurations have been partially located. Combinations involving the transition of one of the inner group of $s^2\ p^2$ electrons have also been detected. A term scheme based on the singlet and triplet series is set up. Interesting cases of interpenetration of the different sub-levels, indicating a strong tendency towards the J J coupling, is pointed out. The largest term $4p\ ^3P_0$ (ν 162788) leads to an ionisation potential of about 20·1 V for the singly ionised atom of arsenic.

Acknowledgments.

My thanks are due to Professor Sir C. V. Raman and to Dr. A. L. Narayan for their continual interest and encouragement, and to Dr. K. R. Rao for very helpful suggetions during the course of the work.

References.

[1] Proc. Phy. Soc., Vol. 44, p. 348 (1932)
[2] *Loc. cit.*
[3] K. R. Rao., Proc. Roy. Soc. (Lond.), Vol. 124, p. 472 (1929).
J. S. Badami and K. R. Rao, Proc. Roy. Soc. (in press).
[4] *Loc. cit.*
[5] A. S. Rao, Current Science, Vol I, No. 2 (1932) and detailed paper in preparation
[6] S. Tolansky, Proc. Roy. Soc. (Lond.), Vol. 137, p. 541 (1932).
[7] Values of the Ionisation Potentials are collected from various papers in the Proc. Roy. Soc. (Lond.) and Phy. Rev.

42

The Raman Spectra of Pinene, Thiophene, Salol and Thymol.

BY

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Plate XXXVI.

ABSTRACT.

The paper describes the results of a study of the Raman effect in pinene, thiophene, molten salol and thymol. In pinene and thiophene, some new frequencies are recorded. Salol and thymol are investigated here for the first time. A brief discussion is given of the prominent features exhibited by the various spectra.

Introduction.

A glass two prism spectrograph is used to photograph the Raman spectra of pinene, thiophene, salol and thymol. The latter two substances are solids at ordinary temperatures and are studied in the molten state. The results are set out in Tables I, II, III and IV ; the letters *a*, *b*, *d*, *e*, *f*, *h*, *i* represent the incident mercury lines λ3650·1, 3654·0, 4046·6, 4077·7, 4339·2, 4358·3 and 5460·7 respectively. Special care is taken to purify the substances by distillation at low pressures with the result that the continuous background arising from fluorescent impurities is very much minimised and good spectrograms of the genuine scattering are obtained.

2. *Discussion of the Results.*

Pinene.—This substance has already been studied by Bonino and Brüll [1] and by Bonino and Cella.[2] In the present paper a number of new lines are recorded. The dextro and laevo modifications exhibit identical frequency shifts and the mean values are given in Table I. The most interesting feature in this case is the presence of a large number of weak and approximately equally spaced frequencies in the region of 1000 to 1450. It has been suggested by Bonino and Cella that these lines have a rotational origin ; the rotator being the CH_2 group. The positions of the various components agree remarkably well with the values calculated by Bonino and Cella. It is, however, strange that all the components, which are more or less equally intense, appear only on one side of the strong C-H frequency 1436. These features present a marked contrast to the usual symmetrical disposition of the rotation patterns on either side of the parent line, their intensity gradually falling off as we recede from the centre. The band in the region of 3000 cm^{-1}, usually ascribed to the C-H oscillations, appears to be very intense in this substance and consists of a large number of components. The existence of an unsaturated $C=C$ bond in the structure of the pinene molecule results in an intense line with a frequency shift of 1661. The frequency 1436 has a peculiar structure in that it

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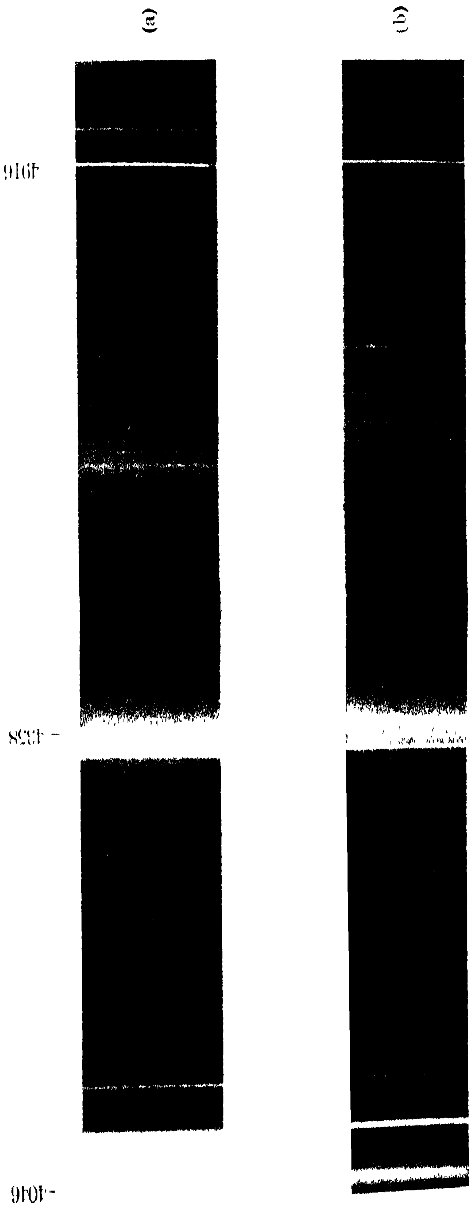
[1] Gazz. Chim. Ital., *59*, 728 (1929).

[2] Nature, *126*, 915 (1930) and Mem. Ital. Acad., *2*, 5 (1931).



(a) Pinene; (b) Molten salol.

RAMAN SPECTRA.

has a sharp edge beginning at 1436 accompanied by a diffuse wing extending up to about 1450.

Thiophene.—This liquid has already been studied by one of us.[8] The results contained in this paper are however more complete and include some new frequencies. The Raman spectrum of this substance is of particular interest as it is one of the few heterocyclic compounds investigated so far. A comparison of its frequencies with those of benzene reveals certain interesting features. The pair of prominent lines 3081 and 3114 in thiophene are no doubt to be regarded as arising from the oscillations of the C-H linkage and the comparatively high value suggests an analogy with the closely spaced frequencies exhibited by benzene and its derivatives in this region. Further, the conspicuous absence of any line in the region lying between 2800 and 3000 also suggests that the C-H linkage in thiophene is distinctively of an aromatic type and has not much in common with those occurring in the aliphatic hydrocarbons.

There is however a marked contrast in another respect between the spectra of benzene and thiophene which may be noted here. A close doublet in the region of 1600 is a very prominent and well-known feature in the spectra of benzene and its derivatives. This has been ascribed by us in our earlier communications to a transverse oscillation of the hydrogen atoms whereas Dadieu and Kohlrausch are of the opinion that it is due to the presence of $C=C$ linkages in the benzene ring. In either case, one should expect the doublet to be present in thiophene as well, but there appears to be no trace of any frequency in this region. In the aliphatic compounds, the frequency of such transverse oscillations is however somewhat lower, and it may be urged that the intense line corresponding to 1408 in thiophene has such an origin. In this connection, a study of the depolarisation values for some of the Raman lines of thiophene given below is of interest.[4]

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[8] S. Venkateswaran, Ind. Jour. Phys., 5, 145 (1930).

Frequency	Depolarisation	Frequency	Depolarisation
452	0·7	1035	0·1
607	0·25	1081	0·3
690	0·8	1361	0·15
752	0·9	1408	0·3
835	0·1	3083	0·9
870	0·9	3111	0·3

Extensive investigations on the depolarisation of the Raman lines in a variety of liquids[5] have shown that the lines corresponding to a frequency of about 1450 in aliphatic compounds and to the close pair of frequencies at about 1600 in aromatic compounds are always depolarised to the maximum extent (0·86) permissible in the theory. Such a high depolarisation is to be expected for transverse oscillations and the results clearly suggest the analogy between the two cases both of which are therefore to be regarded as due to transverse oscillations. Contrary to these very general results, it may be noted from the above table that the line at 1408 in thiophene is sharp, intense and strongly polarised. This line has therefore presumably a different origin, and it is surprising that no frequencies, either of an aliphatic or an aromatic type, can be traced in thiophene which may be attributed to transverse oscillations of the hydrogen atoms.

Salol.—The Raman spectrum of this substance is described here for the first time, and shows some interesting freatures. The intense line at 3076 and the close pair of frequencies 1587 and 1617 are to be attributed respectively to the longitudinal and transverse oscillations of the aromatic C-H bond. It may be noted from the table of polarisation values [6] given below that the latter pair of lines show very nearly the limiting depolarisation as in the case of benzene and its derivatives.

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[4] S. Venkateswaran, Phil. Mag., xv, 263 (1932).

[5] S. Venkateswaran, *loc. cit.*, and L. Simons.

Frequency	Depolarisation	Frequency	Depolarisation
565	0·8	1197	0·6
617	0·8	1250	0·6
675	0·7	1338	0·6
752	0·7	1395	0·7
802	0·6	1467	0·6
844	0·3	1586	0·8
1005	0·2	1617	0·8
1084	0·2	1693	0·5
1136	0·6	3076	0·5
1163	0·6		

A notable feature is the presence of a very intense and fairly well polarised line of a frequency shift of 1693 usually ascribed to the C=O group.

Thymol.—Thymol is also a derivative of benzene, but the presence of alkyl groups in the substitution results in a spectrum which has the characters of both an aliphatic and an aromatic compound as may be seen from the series of high frequencies ranging from 2875 to 3064. The corresponding transverse oscillations are presumably represented by the two lines 1462 and 1620.

The authors desire to express their best thanks to Prof. Sir C. V. Raman for his kind interest in the work.

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[6] S. Venkateswaran, *loc. cit.*

TABLE I.—*Pinene.*

I	ν	$\Delta\nu$	I	ν	$\Delta\nu$
4*d*	24466	*a*−2923	0	22510	*h*−428
4*d*	24431	*a*−2958	0*b*	22466	*h*−472
5	24395	*a*−2994	2	22374	*h*−564
4	24361	*b*−2990	1	22319	*h*−619
0*d*	24266	*d*−179	0	22292	*h*−646
0	24084	*d*−621	4*s*	22272	*h*−666
0	24057	*d*−648	2	22164	*h*−774
3	24038	*d*−667	0	22122	*h*−816
1	23931	*d*−774	3	22094	*h*−844
1	23861	*d*−844	0	22060	*h*−878
0	23827	*d*−878	1	22034	*h*−904
0	29802	*d*−903	0	22006	*h*−933
0	23775	*d*−930	3*b*	21986	*h*−952
2	23758	*d*−947	1	21894	*h*−1044
0	23711	*d*−994	2*s*	21872	*d*−2833
0*b*	23665	*d*−1040	1	21852	*h*−1086
0	23616	*d*−1089	4*b*	21826	*d*−2879
0	23574	*d*−1131	6*b*	21780	*d*−2915
0*b*	23530	*d*−1175	3*b*	21755	*d*−2950
0*b*	23481	*d*−1224	4	21717	*d*−2988
0	23435	*d*−1270	3*b*	21676	*d*−3029
0	23402	*d*−1303	1*b*	21630	*h*−1308
1	23374	*d*−1331	2*b*	21604	*h*−1334
0*d*	23328	*d*−1377	1*b*	21564	*h*−1374
3*dr*	23269	*d*−1436	5*dr*	21502	*h*−1436
0*b*	23071	*h*+133	4*s*	21277	*h*−1661
3*b*	22804	*h*−134	0	20105	*h*−2833
0*d*	22725	*h*−213	2	20064	*h*−2874
2	22677	*h*−261	3*b*	20018	*h*−2920
0	22632	*h*−306	0	19992	*h*−2946
2	22550	*h*−388	0*b*	19948	*h*−2990

$\Delta\nu$:—134 (3*b*), 213 (0*d*), 261 (2), 306 (0), 388 (2), 428 (0), 476 (0*b*), 564 (2), 520 (1), 647 (0). 666 (4s), 774 (2), 816 (0), 844 (2), 878 (0), 904 (1), 931 (0), 949 (3), 994 (0), 1042 (1), 1087 (1), 1131 (0), 1175 (0*b*), 1224 (0*b*), 1270 (0), 1305 (0), 1382 (1), 1375 (0*d*), 1436 (4*dr*), 1661 (4s), 2833 (2), 2876 (4*b*), 2917 (6*b*), 2948 (3*b*), 2989 (4), 3029 (3*b*).

TABLE II.—*Thiophene.*

I	ν	Δν	I	ν	Δν
3	24391	*a*−2998	00	22582	*h*−356
6	24308	*a*−3081	6	22481	*h*−457
10	24275	*a*−3114	0	22433	*f*−606
8	24242	*b*−3112	1	22385	*g*−610
		d−463	1	22368	*h*−570
2	24208	*c*−3085	10	22332	*h*−606
10	24181	*c*−3112	2	22244	*h*−694
10	24101	*d*−604	7	22187	*h*−751
2	24017	*d*−688	2	22161	*g*−834
8	23955	*d*−750	10	22103	*h*−835
2	23910	*e*−606	1	22060	*h*−878
10	23872	*d*−833	1	22031	*h*−907
1	23832	*d*−873	1	21998	*f*−1041
		e−681	3	21955	*f*−1084
2	23800	*d*−995			*g*−1040
2	23771	*e*−745	10	21902	*h*−1036
10	23671	*d*−1034	10	21853	*h*−1085
		e−845	1	21807	*h*−1131
10	23625	*d*−1080	1	21765	*h*−1173
1	23575	*d*−1130	4	21705	*d*−3000
2	23540	*d*−1165	0	21674	*f*−1365
6	23481	*e*−1035	10	21626	*d*−3079
5	23445	*e*−1081	10	21586	*d*−3119
10	23345	*d*−1360			*h*−1352
10	23298	*d*−1407	10	21528	*h*−1410
5	23155	*e*−1361	4	21435	*e*−3081
5	23109	*e*−1407	6	21404	*e*−3112
00	22633	*h*−303	4	19862	*h*−3076

Δν :—303 (00), 356 (00), 457 (0), 570 (00), 606 (10), 690 (2), 751 (8), 834 (10). 875 (1), 906 (2), 1036 (10), 1084 (10), 1131 (1), 1169 (2), 1361 (10), 1408 (10), 2999 (3), 3081 (8), 3114 (10).

TABLE III.—*Salol*

I	ν	$\Delta\nu$	I	ν	$\Delta\nu$
0b	24264	d− 441	2	22462	h− 476
1	24230	d− 475	0	22434	h− 504
0	24202	d− 503	3	22373	h− 565
1	23950	d− 755	0	22321	h− 617
1	23902	d− 803	1	22264	h− 674
4	23860	d− 845	1	22186	h− 752
0	23786	d− 919	1	22136	h− 802
3	23699	d−1006	4	22095	h− 843
4	23672	d−1033	0	22019	h− 919
0	23636	d−1069	4	21934	h−1004
2	23571	d−1134	4	21904	h−1034
3	23543	d−1162	0	21876	h−1062
3b	23506	d−1199	1	21799	h−1139
5	23455	d−1250	3	21775	h−1163
6	23373	d−1332	3	21743	h−1195
1b	23309	d−1396	5	21689	h−1249
4	23238	d−1467	3d	21631	d−3074
1b	23181	e−1335	5	21604	h−1334
3	23119	d−1586	2b	21544	h−1394
2	23090	d−1615	5	21471	h−1467
3	22775	h− 163	3	21350	h−1588
2	22747	h− 191	2	21320	h−1618
2b	22688	h− 250	6b	21245	h−1693
1d	22612	h− 326	1b	19861	h−3077
1	22496	h− 442			

$\Delta\nu$:—163 (3), 191 (2), 250 (2b), 326 (1d), 442 (1), 476 (2), 504 (0), 565 (3), 617 (0), 674 (0), 754 (1), 803 (1), 844 (4), 919 (0), 1005 (4), 1033 (4), 1065 (0), 1136 (2), 1163 (3), 1197 (3), 1250 (5), 1333 (5), 1395 (2b), 1467 (5), 1587 (3), 1617 (2), 1693 (6b), 3076 (3d).

TABLE IV.—*Thymol.*

I	ν	$\Delta\nu$	I	ν	$\Delta\nu$
3	24472	a − 2917	0	22300	f − 739
3	24421	a − 2968	6	22199	h − 739
2	24383	b − 2971	0b	22126	h − 812
		c − 2907	1	22052	h 886
0	24178	d − 527	1b	21991	h − 947
0	24129	d − 576	0	21918	h − 1020
5	23967	d − 738	2	21875	h − 1063
1	23820	d − 885	2	21831	d − 2874
1b	23761	d − 944			h − 1107
0	23692	d − 1013	3b	21777	d − 2928
2	23646	d − 1059	2	21736	d − 2969
0	23593	d − 1112	3	21674	h − 1264
3	23438	d − 1267	1b	21641	d − 3064
1	23325	d − 1380			e − 2875
1b	23244	d − 1461	1	21555	h − 1383
0	22769	h − 169	1b	21474	h − 1461
0	22711	h − 227	2	21318	h − 1620
0	22609	h − 329	3	20062	h − 2876
0	22538	h − 400	2	20015	h − 2923
0	22414	h − 524	1	19969	h − 2969
0	22353	h − 585	0	17565	i − 713

$\Delta\nu$:—169 (0), 227 (0), 329 (0), 400 (0), 525 (0), 580 (0). 739 (6), 886 (1), 946 (1b), 1017 (0), 1061 (2), 1109 (0), 1265 (3), 1381 (1), 1462 (1b), 1620 (2), 2875 (2), 2928 (3b), 2969 (2), 3064 (1b).

Calculation of the Second Virial Coefficient of Gases.

BY

T. S. WHEELER.

(*Received for publication, 2nd Dec., 1932.*)

In a recent paper [1] the author has shown from thermodynamical and dimensional considerations, that the second virial coefficient (B) of a gas consisting of small spherically symmetrical particles, all of one kind, between each pair of which at a distance r from one another there exist two forces given by λ/r^n (repulsive) and μ/r^m (attractive), should be capable of approximate expression by an equation of the form

$$B = C_1 \left(\lambda/T \right)^{3/(n-1)} + C_2 \left(\mu/T \right)^{3/(m-1)} \qquad .(1)$$

C_1 and C_2 are constants and T is the absolute temperature. Lennard-Jones, in a series of classical papers [2] has shown that for the type of gas under consideration,

$$B = (2/3)\pi N \left[(\lambda/(n-1))\ (m-1)/\mu \right]^{3/(n-m)} F(y) \qquad .(2)$$

where N is the number of molecules in the quantity of gas to which B refers, and

$$F(y) = y^{3/(n-m)} \left[\Gamma(n-4)/(n-1) - \sum_{q=1}^{\infty} f(q) y^q \right] \qquad .(3)$$

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[1] Phil. Mag. *13*, 604, 1932.

[2] Proc. Roy. Soc. *112*, 214, 1926.

In this expression,

$$y = [\,\mu/((m-1)\,kT)]\,[((n-1)/\lambda)kT\,]^{(m-1)/(n-1)} \quad \text{...........(4)}$$

and the coefficients $f(q)$ are written for,

$$f(q) = 3\left[\Gamma(\,(q\;\overline{m-1}-3)/(n-1)\,)\right] q\,!(n-1) \quad \text{...........(5)}$$

Lennard-Jones determined by a graphical method values of (m, n) to fit (2) and from these calculated the corresponding values of λ and μ.

It has now been found that the second virial coefficients of the gases considered by Lennard-Jones can be expressed by equations of the type of (1), and that the values of (m, n) which are suitable for (2) are also suitable for (1). Table I shows the application of (1) to the calculation of the second virial coefficients of helium, neon, argon, hydrogen and nitrogen using values of (m, n) chosen from the range given by Lennard-Jones. For nitrogen and argon results obtained by taking (m, n) equal to (4, 9·3) are also given. B refers to 1 c.c. of gas at N. T. P.

The equations employed are as follows :—

Helium (5, 11). $B \times 10^4 = 43{\cdot}5/T^{3/(11-1)} - 193/T^{3/(5-1)}$ ....(6)

Neon (5, 9). $B \times 10^4 = 150/T^{3/(9-1)} - 922/T^{3/(5-1)}$ ....(7)

Argon (5, 9) $B \times 10^4 = 475/T^{3/(9-1)} - 4600/T^{3/(5-1)}$ ....(8)

Argon (4, 9·3). $B \times 10^4 = 251/T^{3/(9{\cdot}3-1)} - 11{,}800/T^{3/(4-1)}$ ......(9)

Hydrogen (5, 9) $B \times 10^4 = 174/T^{3/(9-1)} - 1010/T^{3/(5-1)}$ ......(10)

Nitrogen (5, 9) $B \times 10^4 = 560/T^{3/(9-1)} - 5000/T^{3/(5-1)}$ ......(11)

Nitrogen (4, 9·3) $B \times 10^4 = 298/T^{3/(9.3-1)} - 12{,}000/T^{3/(4-1)}$ ...(12)

It will be seen that the agreement obtained is not unsatisfactory.

TABLE I.

Observed and Calculated Values of B.

Temp.	Helium		Neon		Argon			Hydrogen		Nitrogen		
C°	B′* Obs.	B′ Calc. (6)†	B′ Obs.	B′ Calc. (7)	B′ Obs.	B′ Calc. (8)	B′ Calc. (9)	B′ Obs.	B′ Calc. (10)	B′ Obs.	B′ Calc. (11)	B′ Calc. (12)
−258·0	−6·1	−6·0	...	...	...	...	...	...	...	..	...	...
−208·0	4·2	4·1	...	...	...	...	...	. .	...	..	..	...
−183·0	4·7	4·7	...	...	...	...	...	−2·5	−2·5	..	...	...
−182·5	...	...	−3·7	−3·7	...	...	...	...	...	...	...	...
−150·0	...	...	0	0·3	...	...	...	1·3	1·2	.	..	...
−130·0	...	...	...	...	...	...	...	. .	...	−35·6	−33·5	−34·5
−100	...	...	2·9	2·5	−28·7	−27·4	−28·9	4·1	4·1	−23·1	−23·4	−23·6
− 50	...	...	4·1	3·7	−16·9	−17·2	−17·0	5·4	5·4	−11·8	−13·0	−11·8
0	5·3	5·2	4·8	4·5	− 9·9	−10·6	− 9·8	6·2	6·2	− 4·6	− 6·2	− 4·9
50	5·2	5·2	...	...	− 4·9	− 5·9	− 5·3	6·8	6·7	− 0·1	− 1·5	− 0·6
100	5·1	5·1	5·3	5·5	− 1·9	− 2·4	− 1·8	6·9	7·0	2·7	2·0	2·8
150	...	...	...	...	0·5	− 0·1	0·6	.	...	5·1	4·2	4·9
200	4·9	4·9	5·8	5·8	2·1	2·0	2·5	7·0	7·3	6·8	6·2	6·6
300	4·7	4·7	6·1	5·9	5·0	4·6	5·1		..	9·2	9·2	9·1
400	4·6	4·7	6·1	6·0	6·8	6·3	6·6	...	...	10·5	11·1	10·3

* $B' = B \times 10.^4$ † These numbers refer to the corresponding equations. The observed values of B are taken from the sources used by Lennard-Jones.

The relations involved between (1) and (2) can be deduced as follows :—

Combining (2), (3) and (4) we have,

$$B=(2/3)\pi N\left[\left\{\lambda/(kT(n-1))\right\}^{3/(n-1)}\Gamma\left((n-4)/(n-1)\right)-\right.$$

$$\left.\left\{\lambda/(kT(n-1))\right\}^{3/(n-1)}\left\{\sum_{q=1}^{\infty}f(q)y^{q}\right\}\right]\ldots \qquad \ldots \quad (13)$$

From (13) it is clear that in order that (1) and (2) should correspond Σ and $y^{3/(m-1)}$ should be related by an equation of the first degree over the range of variation of y. Actually a plot of Σ against $y^{3/(5-1)}$ gives a flat curve which approximates to a straight line.

We put therefore in (13),

$$\sum_{q=1}^{\infty}f(q)y^{q}=k_1y^{3/(m-1)}-k_2 \qquad \ldots \qquad \ldots \qquad \ldots \quad (14)$$

where k_1 and k_2 are constants, and obtain,

$$B\doteq(2/3)\pi N\left\{\lambda/(kT(n-1))\right\}^{3/(n-1)}\left\{\Gamma\left((n-4)/(n-1)\right)+k_2\right\}$$

$$-(2/3)\pi N\left\{\mu/(kT(m-1))\right\}^{3/(m-1)}k_1 \qquad \ldots \qquad \ldots \quad (15)$$

$$\text{Since}\int_0^{\infty}x^{-t}e^{-bx^{-q}}dx=(1/q)(b)^{(1-t)/q}\,\Gamma\left((t-1)/q\right) \qquad \ldots \quad (16)$$

we can write (15) in the form

$$B=(2/3)\pi N\int_0^{\infty}(1/kT)\left(\lambda/r^{(n-3)}\right)e^{-\lambda/[(n-1)(kT)\,(r^{(n-1)})]}\,dr$$

$$\left[1+k_2/\Gamma\left((n-4)/(n-1)\right)\right]-$$

$$(2/3)\pi N\int_0^\infty (1/kT)\left(\mu/r^{(m-3)}\right)e^{-\mu/[(m-1)(kT)(r^{(m-1)})]}\,dr$$

$$\left[k_1/\Gamma\left((m-4)/(m-1)\right)\right]\quad\ldots\quad\ldots\quad\ldots\ (17)$$

B is formally expressed by the equation,

$$B=(2/3)\ (\pi N/kT)\int_0^\infty\left(\lambda/r^{(n-3)}-\mu/r^{(m-3)}\right)e^{2jf_1(r)}\,e^{2jf_2(r)}\,dr\ \ldots\ (18)$$

where $2j=1/kT$, ... (19)

and $f_1(r)=-\int_r^\infty\left(\lambda/r^n\right)dr$ ... ... (20)

$$=-\ \lambda\Big/(n-1)r^{(n-1)}\quad\ldots\quad\ldots\quad\ldots\ (21)$$

and $f_2(r)=\mu\Big/(m-1)\,r^{(m-1)}$... ... ... (22)

Hence from (17) and (18) we find that the correspondence of (1) and (2) involves

$$\int_0^\infty\left(\lambda/r^{(n-3)}-\mu/r^{(m-3)}\right)e^{2jf_1(r)}\,e^{2jf_2(r)}\,dr$$

$$\doteqdot\int_0^\infty\lambda/r^{(n-3)}\,e^{2jf_1(r)}\,dr[1+k_2/\Gamma((n-4)/(n-1))]$$

$$-\int_0^\infty\mu/r^{(m-3)}\,e^{-2jf_2(r)}\,dr[k_1/\Gamma((m-4)/(m-1))]\ldots\quad\ldots\ (23)$$

Comparing (15) with (6), (7), (8), (10) and (11), and using Lennard-Jones' values for λ and μ[1] we should obtain values of k_1 and k_2 which for the same values of (m, n) should be independent of the nature of the gas.

TABLE II.

Gas	Helium	Neon	Hydrogen	Argon	Nitrogen
(m, n)	(5, 9)	(5, 9)	(5, 9)	(5, 9)	(5, 9)
k_1	2·71	3·21	3·16	3·53	3·55
k_2	0·24	0·39	0·42	0·60	0·60
(m, n)	$(5, 14\frac{1}{3})$	$(5, 14\frac{1}{3})$	$(5, 14\frac{1}{3})$	$(5, 14\frac{1}{3})$	$(5, 14\frac{1}{3})$
k_1	2·98	3·04	2·92	3·65	3·54
k_2	0·23	0·26	0·26	0·61	0·53

Actually as shown in Table II, for (m, n) equal to (5, 9) and (5, 14·3) the values increase from helium to nitrogen. In considering these variations it should be borne in mind that λ and μ for nitrogen, when (m, n) is equal to (5, 14·3), are, respectively, *1535 and 53 times* as great as the corresponding values for helium. For (m, n), (5, 9), the corresponding ratios are 121 and 35. The greatest change necessary in any of Lennard-Jones' values of λ and μ to obtain constant values of k_1 and k_2 is about 20 per cent. No conclusions can be drawn as to the way in which k_1 and k_2 vary with (m, n).

These maximum differences of the order of 20 per cent. are less than some of the differences obtained by Lennard-Jones between values calculated from the equation of state and from the viscosity measurements. They involve only changes of 2 per cent. in his "generalised diameters" calculated from the formula

$$\sigma_n = (2/3)\,(\lambda/[(n-1)\,(k)])^{1/(n-1)} \qquad (24)$$

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[1] It is interesting to note that for the series of gases considered by Lennard-Jones, log λ plotted against log μ gives a straight line; the slope depends on the value of (m, n) taken.

which he uses for the comparison of various values of λ.

On the whole, therefore, the results of the general dimensional method of approach to the virial problem given by the author in the paper cited are not out of harmony with the more rigorous and definite results of Lennard-Jones.

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Evidence for the Cybotactic Group View of the Interior of a Liquid

By

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(*Received for publication, 3rd Jan., 1933.*)

There is no adequate quantitative theory of the diffraction of x-rays in liquids and chiefly because of the absence of sufficient information concerning molecular structure and intermolecular forces.

Raman and Ramanathan[1] have discussed the fluctuating density in liquids and the consequent coherent interference at small angles of incidence and have, with certain rather severe assumptions, determined the "structural spectrum" of a liquid. This is a constructive and illuminating theory in that it shows what might be expected of symmetrical molecules in a liquid of ordinary density. But the need of the application of a theory to asymmetrical molecules, to liquids at any density and temperature, renders the service of the theory more descriptive than quantitative. Zernike and Prins[2] and subsequently Debye and Menke[3] have pointed out the possibility of obtaining the graph of the probability of distance of separation between one spherical molecule and its neighbours. This is accomplished by using the experimental x-ray diffraction intensity curve. This method is distinctly valuable but of course is not a theory of the phenomena.

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[1] Raman and Ramanathan, Proc. Ind. Assoc. Cult. Sci., VII, II, 127, (1923).

[2] Zs. f. Phys., 41, 184, (1927).

[3] Band II, Ergebnisse der Technischen Röntgenkunde, p. 1, Leipzig, (1931).

It is to be observed that in the above references one begins with the scattering from a single molecule, the first theory mentioned attempting to determine the resulting intensity of diffraction and the last two endeavouring to ascertain what the spacial relation of one molecule to the others actually is. A very different approach has been followed by the laboratory of the author. It is based upon the theory of x-ray diffraction in crystals and assumes that this theory may be applied approximately to molecular aggregates in the liquid. Usually a theory makes internal approximations. In this case the crystal diffraction theory is adopted and then approximations made in its application. It is found experimentally that the intermolecular diffraction in liquids consists of broad bands instead of the sharp lines obtained with crystals, as shown in Fig. 1.[4] This is just what would be expected of molecular aggregates having a semi-orderly or quasi-crystalline array. The groups are small, perhaps of the order of 100 to 1000 molecules, are not sharply defined, are not perfectly regular at any point, and, because of fluctuating density, differ from one another in mean distance of molecular separation. Moreover lack of rigidity of shape of asymmetrical molecules would cause a lack of uniformity. Imposed upon all this is the mobility for the constituency of a group is not permanent, but constantly changing. In short, the quasi-crystalline (cybotactic) structure is unstable. It is further assumed in this view that the peak of the diffraction intensity bands can be used in Bragg's diffraction law to obtain an approximate value of the mean separation of asymmetrical molecules.

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[4] The observations represented by Figs. 1, 2 and 3, were made by using a Mo target, a combination of Zirconium and Strontium filters, producing the practically homogeneous MoKα doublet radiation, and an ionization chamber.

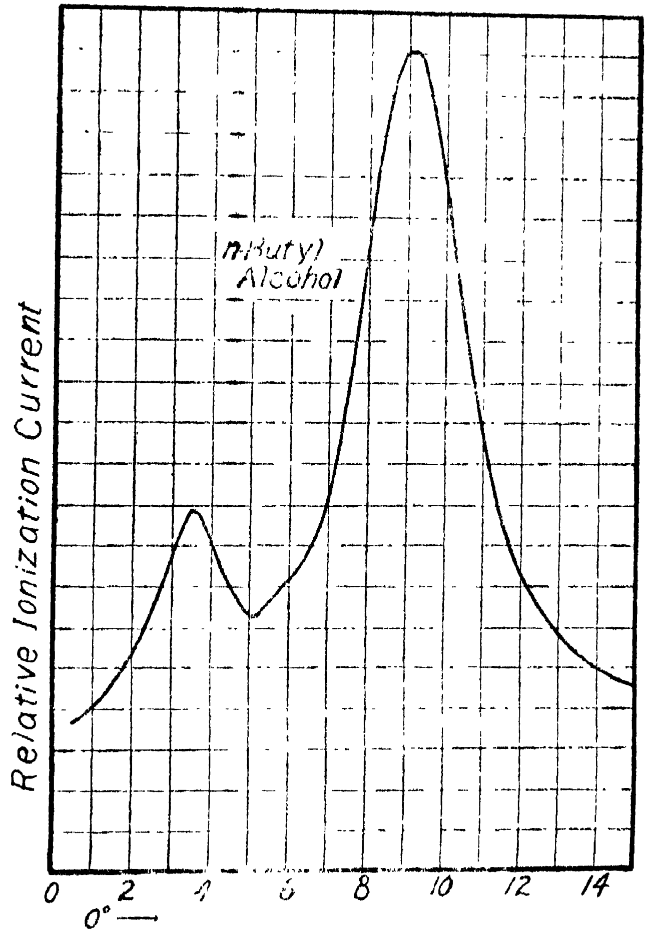

FIG. 1.

X-ray diffraction ionization curve of *n*-butyl alcohol at room temperature.

One would anticipate that the approximations in the application of crystal diffraction theory has its limitations also, since one can pass from a liquid to a gas without any discontinuity. So the author chooses to approach every condition involved from a combination of two approximations to diffraction theory, one that of the crystal and the other that of a random gas condition. With random gas molecules the scattering would be similar to the scattering from random electrons, or proportional to $1 + \cos^2 \theta$, where θ is the angle of scattering. But there is interference in the scattering from the electrons in one molecule and hence the scattering curve shows a sharp decrease with increasing θ as shown in Fig. 2. These approximations do not possess the advantages of an adequate theory, but are justified by effectiveness in explanation and descriptive power, an aspect which is valuable in extending knowledge. One might almost question the application of the term " theory " to this cybotactic view, but as is readily seen, it draws upon the theory of crystal diffraction and of random gas scattering, adds approximations, and thus presents an analogy between the mathematical process and the physical phenomena. It is a constructive but an inadequate theory.

It is to be understood that throughout this paper the classical scattering theory is used, since for the small angles concerned, this theory is satisfactory. But a further step in accuracy beyond what is indicated would be a correction of the experimental observations for the Compton modified scattering.[5] At small angles and Mo Kα radiation this correction is small.

The publications dealing with the cybotactic theory are scattered through the literature of the past five years. It has been suggested that the author collect in a paper for this journal the evidence that has accumulated and which seems to favour the acceptance of the cybotactic condition in liquids as a fact. Obviously such a presentation must be too brief for adequate description of the experimental results and the reader will be obliged to refer to the original papers for a critical examination of the evidence. Moreover, a review of all the experiments in the field cannot be included, for the paper is avowedly a statement of the author's views and the experimental justification for them. An excellent summary with references is to be found in the article by Debye and Menke, to which reference has already been made.

Heisenberg, Physikal. Z. 19, p. 737, 1931 ; Beweilogua, Physikal Z., 19, p. 740, (1931) There is no evidence that opposes the cybotactic view. It is only to be decided whether or not the view has demonstrated its value and is worthy of confidence. Do the temporary semi-orderly groups exist in the liquid ? But before presenting the evidence reference should be made to two suggestions which are to be considered.

It has been shown[6] that if one considers a gas of spherical molecules each having two scattering centres, the typical random gas scattering intensity will be modified by compression

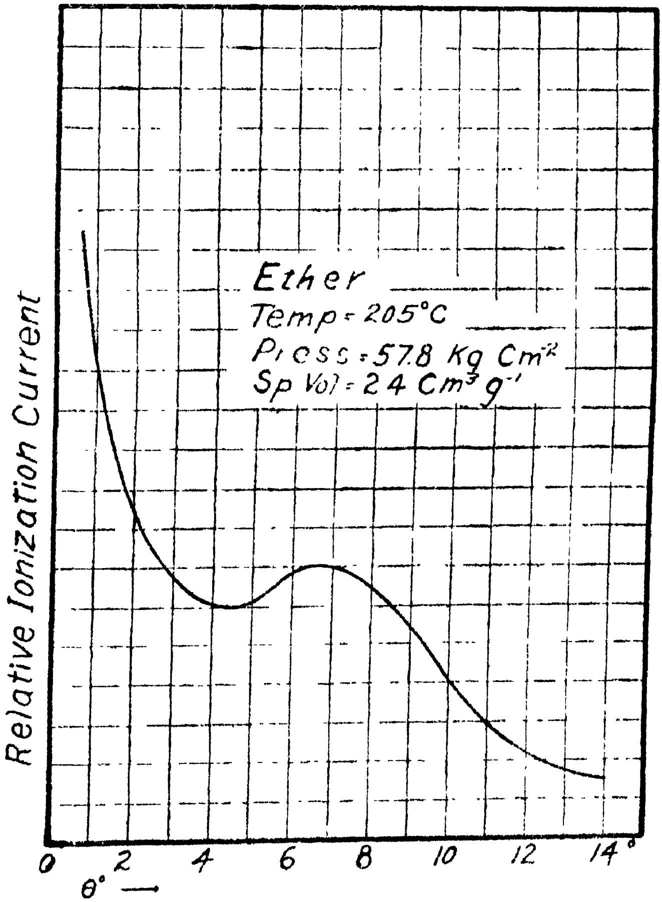

FIG. 2.

X-ray diffraction ionization, showing typical gas curve.

Debye, Jour. of Math. and Phys., 4, 133 (1925) and Physikal Z., 28, 135 (1927).

so that there will be found in the scattering intensity curve a broad peak reminding one of the curves obtained with liquids. It is the magnitude of the fraction of the whole volume occupied by the molecules that determines the presence of this broad peak. As this fraction decreases the peak decreases in size and moves toward the zero angle of diffraction, ultimately disappearing at that angle. The peak is clearly in evidence if the volume occupied by the molecules is one-half of the total volume. The question therefore naturally arises as to whether or not the effect secured in x-ray diffraction in liquids is merely a volume effect. There is the additional suggestion that the shape of the molecules at once compels a preferred orientation. These two suggestions are not contradictory to the group view, but merely are aspects of it. The effect of the molecular forces involved can of course be described in part by a volume and a shape effect, but not adequately by either alone or by both, as will be shown in the evidence. Moreover the very fact that a liquid and vapor may exist in equilibrium, demonstrates that the molecular fields in the liquid are important enough to be really the cause of the existence of the two phases. There is thus no reason for avoiding acknowledgment of an effect of molecular forces at the very outset. Indeed, the more modern view would be to regard any effects of volume and shape as being produced by molecular forces. The discontinuity in passing from liquid to solid rests in the stability and probably not in any alteration of the force functions with temperature.

There will now be cited various experimental results, all of which are readily interpreted in terms of the cybotactic view. The liquid at any instant will be considered, as composed of molecules in small semi-orderly groups, and molecules which are approximately at random as in a gas. Since the purpose of the paper is to present the evidence for this view as clearly as possible consistent with brevity the references to published work will be brief and oftentimes not complete.

1. *A band in the diffraction intensity curve.* A *small* crystal would, as is well-known, give a diffraction band instead of a line, the width of the band depending on the the size of the small crystal. But the lack of constant periodicity in a group would cause an even wider band. Then the periodicity would vary from one point in liquid to another, because of fluctuating density, and this would further widen the diffraction band obtained. There is no difficulty in accounting for the width of the band quantitatively on these grounds. These bands are illustrated in Fig. 1. They are well inside the region of diffraction bands caused by the interference between atoms of same molecule, which is shown in the beautiful experiments of Debye and his students.

2. *Near the zero angle of diffraction.* Coherence in crystal diffraction gives an intensity curve that has practically zero value in the neighbourhood of 0° diffraction angle. *This is roughly true in all liquid experiments* (see Fig. 1), and shows coherence crudely similar to that in a crystal. In most cases there is a small residue of intensity at the nearest approach to 0° (30′ in the author's case) and this is explained by the random molecules. It is readily seen from Fig. 3 wherein the number of random molecules is large, that a small proportion of random molecules would give this effect.

3. *Presence of anisotropy.* A series of n-alcohols [7] and one of n-monobasic fatty acids [8] gives in each case one prominent peak variable in position with the number of carbons in the chain and another practically stationary. This points directly to two different periodicities (or bands), one perpendicular to the chain and one having a component in the direction of the length of the chain. Moreover, *this is precisely what has been found* [9] *with the same fatty acids in solid form.* Indeed, if one uses Bragg's law and the peak of the liquid

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[7] Stewart and Morrow, Phys. Rev., 30, 232, (1927.)

[8] Morrow, Phys, Rev., 31, 10, (1928).

[9] Gibbs, Jour. Chem. Soc. London, 125 2622, (1924)

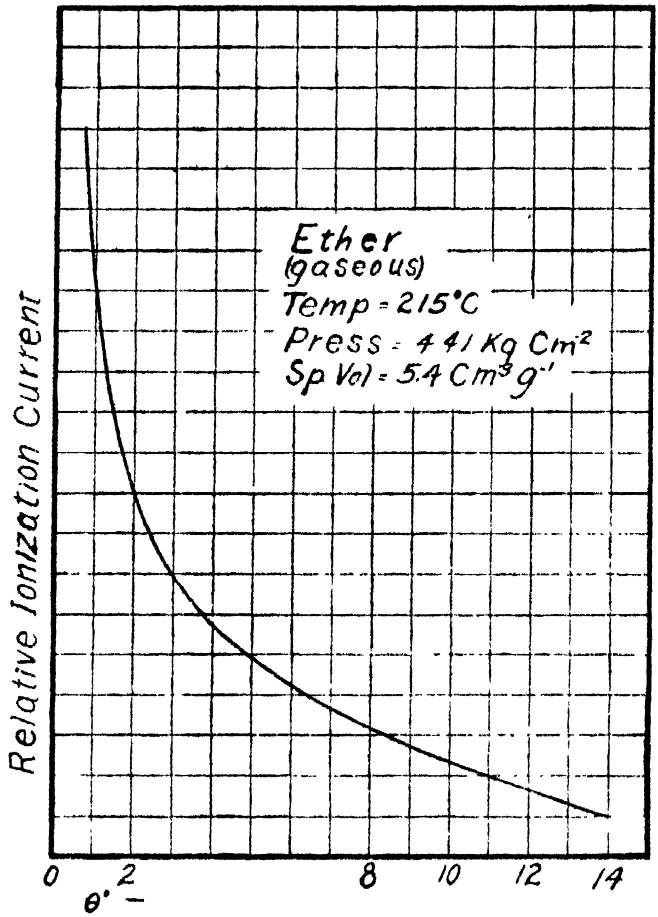

FIG. 3.

X-ray diffraction ionization curve of ethyl ether at a pressure and temperature above the critical values, 194·6°C and 36·7 *kg/cm*$^{-2}$ respectively.

intensity curve to compute the mean periodicity, *the periodicity and the rate of change of this peridicity with the number of carbon atoms are approximately the same in the liquid and solid states.*

4. *Measurement of length occupied by a carbon atom in a hydrocarbon chain.* Computations from observations on liquid in paraffins [10] give the length 1·24 Å. u. as that occupied by the carbon atom, or the CH_2, along the chain. This is in

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[10] Stewart, Phys. Rev., 31, 174, (1928).

agreement with the results of Müller and Saville [11] and Piper, Brown and Dyment [12] with solid hydrocarbons, the former obtaining a value of 1·3 Å. u., and the latter 1·22 Å. u. Moreover the distance of separation in the diamond along a line is 1·26 Å. u.

5. *Comparison with molecular dimensions in a surface film.* The area occupied by the cross-section of a molecule of normal monobasic acids in a surface-film in water as found by Adam [13] is 21×10^{-16} cm^2. The cross-sectional area found by Morrow (*loc. cit.*) for the same acids in the interior of the liquid, assuming groups, is $(4{\cdot}57 \times 10^{-8}\ \text{cm.})^2 = 20{\cdot}9 \times 10^{-16}\ \text{cm}^2$ and by Stewart and Morrow (*loc. cit.*) for n-alcohols, is $(4{\cdot}58 \times 10^{-8}\ \text{cm})^2 = 21 \times 10^{-16}\ \text{cm}^2$. The cybotactic view is thus in harmony with surface film measurements.

6. *Comparison of crystalline and liquid diffraction curves.* Numerous comparisons have been made[14] of the two diffraction curves. Always there appears a chief diffraction band with the liquid at an angle approximately the same as the chief line or group of lines with the crystal. The expriments are similar, one with liquid and the other with powdered crystal, and the similarity in coherence diffraction, although crude, is what would be anticipated from the cybotactic view. [15]

7. *Comparison of liquid and solid solutions.* Binary solutions, where the components are miscible, show not the intensity maxima of both components, but a modification as of a single liquid. [16] This is similar to the well-known case of a

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[11] Müller and Saville, Jour. Chem. Soc., 27, 599, 1925.

[12] Piper, Brown and Dyment, Chem. Soc. Jour., 127, 2194, 1925.

[13] Adam, Proc. Roy. Soc. 99A, 336 (1921), 101A, 452, 456, (1922), 103A, 676, 687 (1923).

[14] E.g., Krishnamurti, Ind. Jour. Phys., 3, 225 (1928), and also Stewart and Morrow, (*loc. cit.*) and Morrow (*loc. cit.*).

[15] A preliminary announcement has just been made by J. T. Randall and H. B. Rooksby in Nature of September 24th, 1932, of similar comparisons made between the crystal and liquid conditions of the metals, sodium, potassium, rubidium and caesium.

[16] Krishnamurti, Ind. Jour. Phys., 3, 331, 1929 Hertlein, Z. f. Phys. 54, 341, 1921, and Meyer, A. W. Phys. Rev., 38, 1038, 1931.

solid solution. In fact the change in dimensions with concentration obtained from the liquid diffraction peak is exactly like that occurring when the two solids of similar crystal structure from a solid solution. This is readily explicable on the basis of the cybotactic view and similarity to the crystalline condition. The molecules of the solute participate in the space array of the solvent. This view of a solution is very helpful.

8. *Simultaneous determination of two or three periodicities.*—The measurement of two independent periodicities have been mentioned in "3" above. Di-n-propyl carbinol[17] gives three peaks which correspond to distances of 10·5, 4·85 and 4·5 Å. u. These distances are in distinct harmony with the expected structure of the molecule, the group OH being in a branch. Numerous other three-peak curves have been found where the distances must be between and not within the molecules. More than one distance shows that the x-ray effect is not caused by a statistically mean distance of separation, and *that there is actually an anisotropy which is satisfied only by a structure.*

9. *Change in molecular diameter by alteration in molecular structure.*—In a series of n-alcohol and n-paraffin isomers[18] and in a series of twenty-one octyl alcohols[19] the influence of CH_3 and OH in branch lines is plainly evident, and in quantitative agreement with current views of molecular structure.

10. *Effect of temperature.*—The influence of temperature upon the position of the maxima and the breadth of the peak is similar to that with powdered crystals, namely, a shift to smaller angles, and a broadening of the peak. In addition there is an increase in intensity with angles near the 0°.

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[17] Stewart and Skinner, Phys. Rev., 31, 1 (1928).

[18] Stewart and Skinner, Phys. Rev., 31, 1, 1928 and Stewart, Phys. Rev. 32, 153, 1928

[19] Stewart, Phys. Rev., 35, 726, 1930.

All of this is explicable by the cybotactic view, the "random" molecules increasing in number with increasing temperature.

11. *Computation of relative intensities from the structure factor.*—The diffraction curves with n-alcohols have already been described. Spangler[20] has computed the relative intensities of the two peaks to be as expected on the cybotactic view of the group structure of the n-alcohols from methyl to lauryl and finds that the agreement is excellent. Moreover he finds that the second order maximum would have too small an intensity to be in evidence, and this is experimentally the case also. These are quantitative verifications of the group conception.

12. *Molecules of approximately the same shape and volume, but widely different diffraction intensity curves.* Reference has already been made to the diffraction intensity curves for n-paraffins and n-alcohols. These two compounds differ only at the end of the chain, one having CH_3 and the other OH. Evidently the moleclules of these homologous series, when otherwise alike, should have very closely the same volume and shape. Yet the diffraction intensity curves are clearly different, the alcohols having an inner maximum as shown in Fig. 1. The difference is simply explained in the cybotactic view by the second periodicity in the n-alcohols doubtless produced in part by its polarity. But consider two polar compounds having the same molecular constitution but differing slightly in the position of the OH group, secondary amyl alcohol and diethyl carbinol. Five carbons are in each chain, but in one the OH is attached at 2, while in the other it is attached at 3. Yet the inner peaks represent the different periodicities[21] of 11·3 and 8·9 Å. u., respectively. There are numerous other cases showing that a consideration only of volume and shape is inadequate. The molecular grouping in semi-orderly array seems always a satisfactory view.

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[20] Spangler, Radiology, XVI, 359, 1931.

[21] Stewart and Skinner, Phys. Rev., 31, 1, 1928.

13. *Evidence near the critical point.*—From the as yet unpublished observations on ethyl ether of Noll and Spangler of this laboratory it seems to be established that the group exist in the liquid but not in the vapor, apparently disappearing at the critical point. This was anticipated from the cybotactic view.

14. *Continuous passage from gas to liquid.*—The term liquid is usually limited to the denser fluid in the two phase region which possesses a surface and does not fill the vessel. But, from the cybotactic view, one sees the grouping of molecules as occurring outside this two-phase region. The recent work referred to in the preceding paragraph shows that at specific volumes less than that at the critical point, groups exist (Fig. 3). The extent of the groups depends most importantly on the specific volume. This new information concerning the interior gives a new conception of the nature of the gradual change from a region where no groups exist to the liquid state. It should be remarked, however, that when the specific volume is increased the peak disappears without the movement toward 0° mentioned in the case of the theoretical discussion by Debye of the effect of volume. While it is true that Debye's theory cannot be extended to the present case, yet it is reasonable to expect that an adequate volume-effect theory would show a vanishing of the peak in the intensity curve simultaneously as it approaches $\theta = 0^\circ$.

15. *The "quasi-crystalline" condition of liquid mercury and gallium.*—By diffraction at the surface of mercury and the application of the theory already mentioned, Debye and Menke[22] have shown that there is a quasi-crystalline structure of the surface of mercury and Menke[23] in the surface of liquid gallium. In fact the probability of separation of one molecule from its neighbours is a crude imitation of this probability in

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[22] Debye and Menke, *loc. cit.*

[23] Menke, Physikal Z, 16, p. 393, 1932.

a simple crystal. Of course the experiments refer to the surface condition of monatomic liquids and not to the interior, but one may with safety assume the correctness of the conclusions for the interior. It is especially to be noted that the structure of these two monatomic liquids differ somewhat, that of Hg being more marked. It is evident that even here with atoms, the most symmetrical units, the molecular forces cannot be overlooked, and the explanation cannot be secured by a volume effect only. All this emphasizes the soundness of the cybotactic view as applied to liquids in general.

These fifteen experimental results just cited are, without exception, in accord with the cybotactic view which regards the liquid as consisting of aggregates which crudely simulate crystalline orderliness and of molecules which are approximately at random. This view or theory is much more than an interesting description. It has been valuable, for example, in giving a clearer insight into the nature of a solution of miscible liquids and into the effect of pressure in forming these liquid aggregates at temperatures and pressures above the critical values. Undoubtedly it will in the future help to add to our understanding of the nature of electrolysis as well as many aspects of solutions. It has been shown in the foregoing that explanations of the x-ray diffraction phenomena based upon either the volume or the shape of the molecule or by both, are inadequate. These two aspects are only part of the whole effect of molecular forces. The stable configuration in crystals should long ago have urged upon us a revision of our conception of the liquid state.

45

Electric Polarisability and Diamagnetic Susceptibility of Molecules.

By

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ABSTRACT.

A relation between the electric polarisability and the diamagnetic susceptibility of atoms, deduced by Vinti, has been tentatively applied to simple molecules. In place of the usual Langevin-Pauli formula for the diamagnetic susceptibility of atoms, use is made of the fuller expression given by Van Vleck for molecules. The latter is characterised by the presence of a feeble paramagnetic term and the results show that its numerical value increases with increasing asymmetry of the molecule. The parallelism is to be expected theoretically.

The polarisability a of an N electron atom has been expressed by Vinti in a recent paper [1] by the relation

$$a=\frac{16\pi^2e^2m}{9h^2\mathrm{N}}\left\{\sum_{i=1}^{\mathrm{N}}(r_i^2)_{00}+\sigma\right\}^2 \qquad \dots \quad (1)$$

The various letters have the usual significance. He has also shown that the parameter σ may in general be neglected in comparison with the first term. If, in this equation, the value of $\sum_{i=1}^{\mathrm{N}}(r_i^2)_{00}$ deduced from the usual Pauli-Langevin formula

$$\chi=-\frac{e^2\mathrm{L}}{6mc^2}\sum_{i=1}^{\mathrm{N}}(r_i^2)_{00} \qquad \dots \quad (2)$$

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[1] Phys. Rev., 41, 813 (1932).

is substituted, the following relation connecting the diamagnetic susceptibility and the electric polarisability results.

$$-\chi=(c^2a_0^{1/2} \Big/ 4\,mc^2)\quad(\mathrm{N}\alpha)^{1/2} \qquad \ldots \quad (3)$$

Here a_0 stands for the radius of the first Bohr orbit. The relation is rigorously valid only for atoms but a tentative application of this to simple molecules will be made in the present paper. In this case, the relation will naturally be expected to be only of approximate validity as neither the magnetic nor the optical anisotropy of the molecules has been taken account of in its derivation. We will therefore regard χ and α as representing the average values of the principal susceptibilities and the polarisabilities respectively. It must however be remarked that the average polarisability of a molecule may be expected to be somewhat larger than the sum of the individual polarisabilities of the constituent atoms[2] and thus the value of α calculated with the help of equation (3) will apparently be increased. Such an increase in the average polarisability due to molecule formation is only of the order of about 10% even in highly anisotropic molecules and this would cause an apparent increase of about 5% in the value of α as the polarisability enters under a square root in equation (3). It will be seen later that this does not affect the main conclusion of the present paper.

In applying the above relation to molecules one should, in the place of the Langevin-Pauli formula, use the fuller expression

$$\chi=-\frac{\mathrm{L}c^2}{6m\,c^2}\sum_{i=1}^{\mathrm{N}}(r_i^2)_{00}+\frac{2}{3}\,\mathrm{L}\sum_{n'\neq n}\frac{|\,m_0(n';\,n)\,|^2}{h\nu(n';\,n)} \qquad \ldots \quad (4)$$

given by Van Vleck[3] for the molal diamagnetic susceptibility of polyatomic molecules. The second term in equation (4) is characteristic of molecules and indicates the presence, in these cases, of a feeble paramagnetism independent of temperature. Denoting this term by C, we have the relation

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[2] K. R. Ramanathan, Proc. Roy. Soc., **107**, 684 (1924).

[3] *Theory of Electric and Magnetic Susceptibilities*, p. 275 (1932).

$$\sum_{i=0}^{N} (r_i^2)_{00} = (C-\chi)\,\frac{6m\,c^2}{Lc^2}.$$

Substituting this in equation (1) and neglecting σ as before we obtain

$$C-\chi = (e^2a_0)^{1/2}\ L/4m\,c^2)\ (N)^{1/2} \tag{5}$$

for molecules in place of equation (3) of atoms. In this equation, χ represents the actual molal diamagnetic susceptibility of the gas and it can be numerically evaluated only if the value of C is known. A direct theoretical computation of this term is very difficult even in simple cases and as such it has so far been done only for hydrogen.[4] On the other hand if we substitute the known diamagnetic susceptibilities for χ in equation (5), the value of C may in each case be deduced. This has been done in the following Table for some simple molecules so chosen as to bring out the essential features.

TABLE I.

Gas	N	$\alpha \times 10^{24}$	$\chi \times 10^6$	C (Calc.)	$\rho \times 10^2$	γ
H_2	2	0·818	3·99	0	2·57	1·00
N_2	14	1·748	12·9	2·5	3·55	0·63
CO_2	22	2·642	18·7	5·0	9·72	0·56
N_2O	22	2·988	18·9	6·3	12·47	0·34

The diamagnetic susceptibilities for H_2, CO_2 and N_2O are due to Soné, whereas the one for nitrogen is due to Vaidyanathan. Different observers have obtained values ranging from 10×10^{-6} to about 15×10^{-6} for nitrogen and hence this mean value is selected. Bitter[5] has recently reported a very high value for H_2 and a correspondingly large susceptibility for CO_2 and N_2 but he obtains a somewhat surprising and unexpected result in that the susceptibility of H_2 comes down according to him to the normal value ($3{\cdot}3 \times 10^{-6}$) at low temperatures. In view of the uncertainty involved, his results are not included in the Table. ρ is the depolarisation of the light scattered transversely by these gases and γ is the anomaly in the Verdet's constant.

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[4] J. H. Van Vleck and A. Frank., Proc. Nat. Acad., 15, 539 (1929).

It is to be noted that the value of C comes out as zero in hydrogen suggesting that the hydrogen molecule approaches very closely to atomic symmetry.[6] This result has already been noted by Van Vleck and by Serber[7] as this alone, of all the molecules, exhibits a normal Faraday rotation in the sense that the classical Becquerel formula, which may be expected to be valid only for atoms, is applicable without any modifications in this case.

It is also noteworthy that the value of C, both absolutely and when expressed as a fraction of the actual susceptibility, increases as we pass from H_2 to N_2 to CO_2 and N_2O. In the last named compound its value is over 30% of the actual susceptibility. That this is also the order of increasing asymmetry of the molecules is clearly borne out by the figures given in column 6 of the Table. These figures represent the depolarisation of the light transversely scattered by the gases and afford a measure of the optical asymmetry of the respective molecules. The increasing non-monatomic character of this series is also brought to light by the figures for the anomaly in the Faraday rotation given in the last column. The origin of such a paramagnetic term in molecules has been investigated by Van Vleck and its existence is due to nuclear fields which do not possess central symmetry. That it should be large in unsymmetrical molecules is therefore to be expected and the results are in accordance with such an expectation.

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[5] Phys. Rev., 36, 1648 (1930).

[6] Such a perfect agreement with the atomic formula is probably partly accidental as Van Vleck and Miss Frank (*loc. cit.*) have found that this term has a finite, although small (about 10% of the Langevin-Pauli term), value in H_2. It is however certain that its value in this case is very small.

[7] Phys. Rev., 41, 489 (1932).

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